21st Topical Meeting
of the International Society of Electrochemistry

Photoelectrochemistry of semiconductors
at the nanoscale: from fundamental aspects
to practical applications

23-26 April 2017, Szeged, Hungary

PROGRAM

View all ABSTRACTS and
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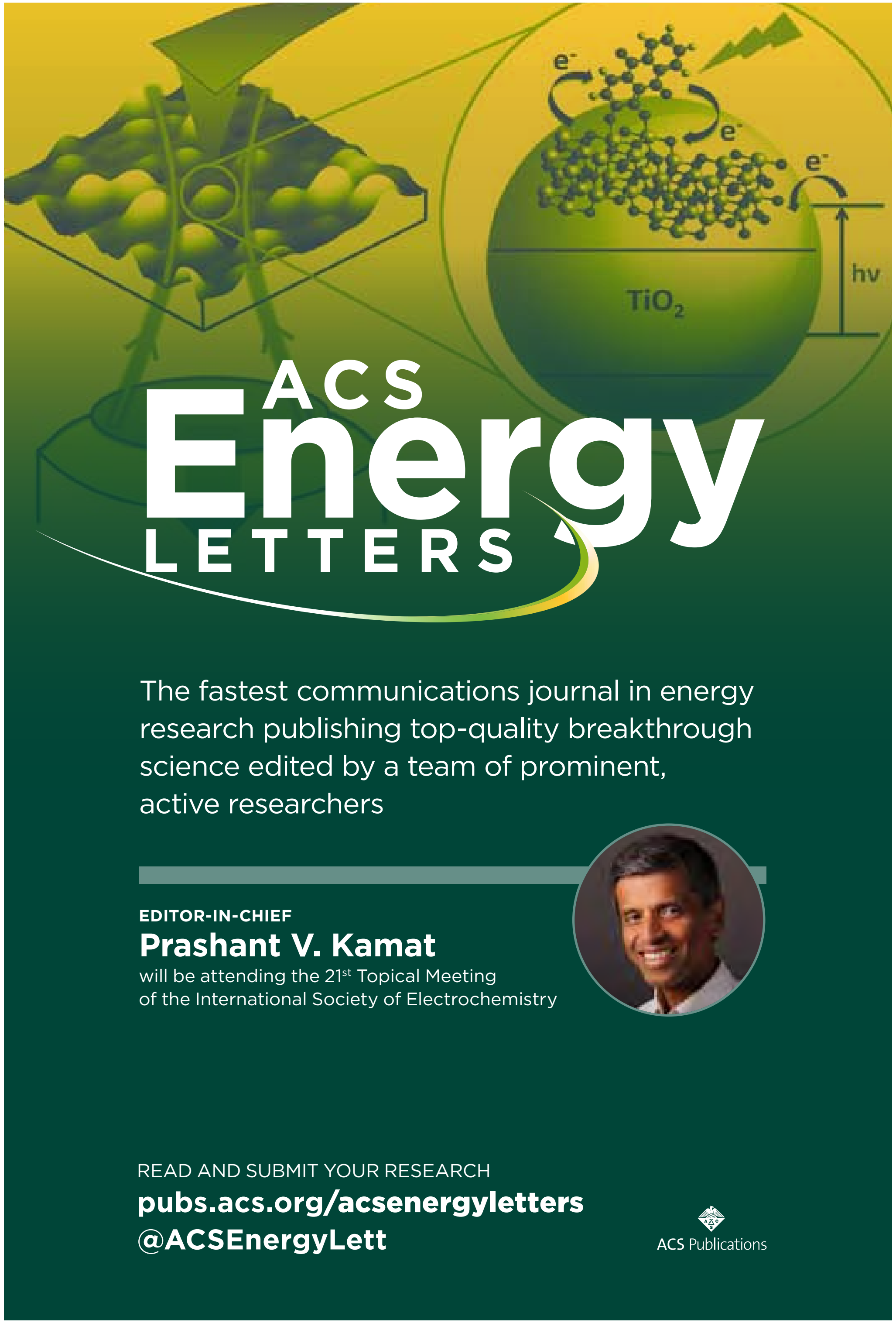
the ISE Conference APP

Conference Schedule

	Sunday	Monday	Monday	Tuesday	Tuesday	Wednesday	Wednesday
08:20-09:20		Keynote		Keynote		Keynote	
09:20-09:40		Invited Oral Oral	Invited Oral Oral	Invited Oral Oral	Invited Oral Oral	Invited Oral Oral	Invited Oral Oral
09:40-10:00							
10:00-10:20							
10:20-10:40							
10:40-11:00		Coffee break		Coffee break		Coffee break	
11:00-11:20		Oral	Oral	Oral	Oral	Oral	Oral
11:20-11:40							
11:40-12:00							
12:00-12:20							
12:20-12:40		Lunch	Lunch	Lunch		Closing ceremony	
12:40-13:00							
13:00-13:20				Poster Session 2		Lunch	
13:20-13:40							
13:40-14:00							
14:00-14:40			Invited Oral				
14:40-15:00	Registration	Oral	Oral	Visit at the Extreme Light Infra-structure - Attosecond Light Pulses (ELI-ALPS) and City tour or alternatively visit to Ópusztaszer			
15:00-15:20							
15:20-15:40							
15:40-16:00							
16:00-16:20		Coffee break					
16:20-16:40		Oral	Oral				
16:40-17:00							
17:00-17:20							
17:20-17:40							
17:40-18:00	Opening ceremony	Poster Session 1 & Wine tasing					
18:00-18:20	Keynote						
18:20-18:40							
19:00-20:00	Welcome Reception at the Town Hall	Dinner		Banquet			
19:20-19:40							

- New Materials
- Novel Characterization Tools
- Emerging Applications
- Synthesis of Semiconductor Electrodes
- Solar Fuels



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Prashant V. Kamat
will be attending the 21st Topical Meeting
of the International Society of Electrochemistry

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Program of the

21st Topical Meeting of the International Society of Electrochemistry

Photoelectrochemistry of semiconductors at the nanoscale: from fundamental aspects to practical applications

23-26 April 2017
Szeged, Hungary

Organized by:
Division 6 Molecular Electrochemistry
Division 7 Physical Electrochemistry
ISE Region Hungary

International Society of Electrochemistry
Chemin du Closelet 2
1006 Lausanne
Switzerland

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Tamas Pajkossy, *Electrochemistry Committee of the Hungarian Academy of Sciences, Hungary*
Csaba Visy, *University of Szeged, Hungary*

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Sunday 23 April 2017

Opening Ceremony

Room : Juhasz Gyula Terem

17:45

Chaired by: Csaba Visy, László Peter

Keynote

Room : Juhasz Gyula Terem

Chaired by: Krishnan Rajeshwar

18:00 to 18:55 Keynote

Akira Fujishima (Tokyo University of Science, Tokyo, Japan)

TiO_2 Photocatalysis and Diamond Electrode

Sunday 23 April 2017

Welcome Reception

Sponsored by the City of Szeged

19:30

Town Hall Szeged

approximately 28 minutes walking

Directions from Hunguest Hotel Forrás to Town Hall, Széchenyi Tér, 6720 Szeged

Hunguest Hotel Forrás, Szent-Györgyi Albert u. 16

- Head west on Szent-Györgyi Albert u. toward Fürdő u. ➠ 250 m
- Turn right onto Népkert sor ➠ 30 m
- Continue onto Szent-Györgyi Albert u. ➠ 66 m
- Turn right onto Belvárosi híd ➠ 550 m
- Continue onto Híd u. ➠ 260 m
- Turn right onto Széchenyi tér ➠ 58 m
- Turn left to stay on Széchenyi tér ➠ 140 m
- Turn right to stay on Széchenyi tér ➠ 50 m
- Turn left to stay on Széchenyi tér
- Destination will be on the right ➠ 36 m

City Hall Szeged, Széchenyi tér 10, 6720 Hungary
Welcome address by Dr. Ottó Berkesi, elected member of the City Council

Monday 24 April 2017 - Morning

Keynote

Room : Juhasz Gyula Terem

Chaired by: Laurie Peter

08:20 to 09:15 Keynote

Prashant V. Kamat (Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, USA), Jacob Hoffman, Seog Joon Yoon

Perovskite Solar Cells. Intricacies of Light Induced Processes

Solar Fuels

Room : Juhasz Gyula Terem

Chaired by: Akira Fujishima and Hyunwoong Park

09:20 to 10:00 Invited

Pawel J. Kulesza (Department of Chemistry, University of Warsaw, Warsaw, Poland), Krzysztof Bienkowski, Aneta Januszewska, Rafal Jurczakowski, Iwona A. Rutkowska, Ewelina Seta, Katarzyna Skorupska, Krzysztof Slojewski, Renata Solarska, Ewelina Szaniawska, Anna Wadas, Sylwia Zoladek

Hybrid and Functionalized Interfaces for Photoelectrochemical and Electrocatalytic Reduction of Carbon Dioxide

10:00 to 10:20

A. Wouter Maijenburg (ZIK SiLi-nano, MLU Halle-Wittenberg, Halle (Saale), Germany)

Nanostructure Design for Photocatalytic Water Splitting

10:20 to 10:40

Petr Krtil (Low Dimension Systems, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic), Ivano Castelli, Ladislav Kavan, Monika Klusackova, Katerina Minhová Macounová, Roman Nebel, Jan Rossmeisl

The Role of Anatase Surface Orientation in Selectivity of Photo-electrochemical Water Splitting

10:40 to 11:00

Coffee Break

11:00 to 11:20

Bruno Fabre (Institut des Sciences Chimiques de Rennes UMR6226, University of Rennes 1, Rennes, France), Sylvie Chardon, Encarnación Torralba Peñalver

Light-Driven Electrocatalytic Reduction of CO_2 on Silicon Nanowires using Mn Bipyridyl Complex Catalysts

11:20 to 11:40

Attila Kormányos (Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary), Dorottya Hursán, Csaba Janáky, Egon Kecsenovity

Photoelectrochemical Reduction of CO_2 on Organic/inorganic Nanocomposite Photoelectrodes

11:40 to 12:00

Nestor Eduardo Mendieta Reyes (Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia), Ana Korina Díaz García, Roberto Gómez, Carlos Alberto Guerrero Fajardo

Study of electrochemical CO_2 reduction over WO_3 electrodes in aprotic media

Synthesis of Semiconductor Electrodes

Room : Szent-Gyorgyi Albert Terem

Chaired by: Pawel J. Kulesza and Ladislav Kavan

09:20 to 10:00 Invited

Wojciech Macyk (Faculty of Chemistry, Jagiellonian University, Kraków, Poland), Marta Buchalska, Marcin Kobielusz, Michal Pacia, Mateusz Trochowski

Analysis and engineering of electronic states in semiconductor photocatalysts

10:00 to 10:20

Jan Macak (Center of Materials and Nanotechnologies, University of Pardubice, Pardubice, Czech Republic), Milos Krbal, Siowwoon Ng, Jan Prikryl, Hanna Sopha, Raul Zazpe

Enhanced Photoelectrochemical Efficiency of Self-Organized TiO_2 Nanotube Layers due to Secondary Materials

10:20 to 10:40

Leszek Zaraska (Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Krakow, Poland), Karolina Gawlak, Dominika Gilek, Krystyna Mika, Grzegorz D. Sulka, Karolina Syrek, Marta Zych

Anodic oxidation as a simple and cost-effective method for fabrication of nanostructured semiconductor oxides with various morphologies

10:40 to 11:00

Coffee Break

11:00 to 11:20

Joanna Kuncewicz (Faculty of Chemistry, Jagiellonian University in Kraków, Kraków, Poland), Bunsho Ohtani

Rhodium-doped Titania: The Effect of the Doping Conditions on Bands Position and Density of Introduced Electronic States

11:20 to 11:40

Balazs Endrodi (Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary), Csaba Janáky, Egon Kecsenovity

Development of a Rapid, One-step Electrodeposition Method Resulting in Nanocrystalline TiO_2 Films with Enhanced (Photo)electrochemical Performance

11:40 to 12:00

Tso-Fu Mark Chang (Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Japan)

Effect of Applied Pressure on Photocatalytic Activity of Titanium Dioxide Synthesized by Cathodic Deposition with Supercritical Carbon Dioxide

12:00 to 12:20

Marta Michalska-Domanska (Institute of Optoelectronics, Military University of Technology, Warsaw, Poland), Mateusz Czerwinski, Piotr Nyga

Effect of water content in electrolyte on anodic titanium oxide morphology and optical properties

Monday 24 April 2017 - Afternoon

Synthesis of Semiconductor Electrodes

Room : Juhasz Gyula Terem

Chaired by: Nathan Lewis

14:00 to 14:40 Invited

Bunsho Ohtani (Institute for Catalysis, Hokkaido University, Sapporo, Japan)

Why should Photocatalysts be Semiconductor? - Roles of Electron Traps in Metal Oxide Particles

Room : Szent-Gyorgyi Albert Terem

Chaired by: Wojciech Macyk

14:40 to 15:00

Andrés G. Muñoz (Process Analysis, Gesellschaft für Anlagen- und Reaktorsicherheit GRS gGmbH, Braunschweig, Germany), Laura Beuth, Anja Dobrich, Thomas Hannappel, Hans-Joachim Lewerenz, Matthias M. May, Heike Mönig

Photo-electrodeposition of Rhodium on III-V Semiconductors for the Construction of Tandem Water Splitting Devices

15:00 to 15:20

Cheryl Karman (Laboratoire Chimie Physique Microbiologie pour Environnement, Universite de Lorraine, Villers-les-Nancy, France), Alonso Gamero-Quijano, Grégoire Herzog, Neus Vilà, Alain Walcarius

Controlling the Growth of Electropolymerized Polyaniline Nanorods through Vertically Oriented Silica Mesostructures

15:20 to 15:40

Gergely Samu (Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary), Csaba Janáky, Krishnan Rajeshwar, Swagotom Sarker, Vaidyanathan Subramanian, Csaba Visy

Photoelectrochemical synthesis of conducting polymer/inorganic semiconductor assemblies

15:40 to 16:00

Dwight Acosta (Condensed Matter Department, National University, Ciudad de México, Mexico), Francisco Hernández

The influence of applied voltage and solution temperature on physical properties of electrodeposited ZnO thin films

16:00 to 16:20

Coffee Break

Emerging Applications

Room : Juhasz Gyula Terem

Chaired by: Bunsho Ohtani and Hyunjung Shin

14:40 to 15:00

Ladislav Kavan (Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic), Petr Cigler, Hana Krysova, Vincent Mortet, Zuzana Vlckova-Zivcova

Boron-Doped Diamond Electrodes for Dye-Sensitized Solar Cells

15:00 to 15:20

Kai Yan (School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, China), Yaohua Yang, Jingdong Zhang

The Application of Photofuel Cells in Self-powered Sensing Platforms

15:20 to 15:40

Karolien De Wael (Chemistry, Antwerp University, Antwerp, Belgium)

Molecular Photosensitizers: Emerging (Bio)Analytical Sensing Tools

15:40 to 16:00

Kristina Wedege (Chemical and Biological Engineering, Aarhus University, Aarhus C, Denmark), João Azevedo, Anders Bentien, Amirreza Khataee, Adélio Mendes

Photoelectrochemical Charging of an Aqueous Flow Battery by a Polyaniline Surface-treated Hematite Photoanode

16:00 to 16:20

Coffee Break

16:20 to 16:40

Hsin-Fu Yu (Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan), Kuo-Chuan Ho, Sheng-Yuan Kao, Man-kit Leung, You-Shiang Lin

A high contrast complementary electrochromic device based on two conducting polymer thin films

16:40 to 17:00

Omotayo Arotiba (Applied Chemistry, University of Johannesburg, Johannesburg, South Africa), Jane Ngila, Moses Peleyeju, Eseoghene Umukoro

Towards Wastewater Treatment: Photo-assisted Electrochemical Degradation of Nitrophenol and Orange II dye at a Tungsten Trioxide-Exfoliated Graphite Nanocomposite Electrode

17:00 to 17:20

Iryna Sagaidak (Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, Amiens, France), Christian Andriamiadamanana, Gaspard Bouteau, Christel Laberty-Robert, Albert Nguyen Van Nhien, Frederic Sauvage

Ionic transfer triggered by light action: a case of TiO_2 nanocrystals towards photonic Li-ion battery

17:20 to 17:40

Valentina Pifferi (Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy), Silvia Ardizzone, Michele Ceotto, Giovanni Di Liberto, Luigi Falciola, Leonardo Lo Presti, Daniela Meroni, Guido Panzarasa, Guido Soliveri

Silver Nanoparticles/Nanostructured TiO_2 Interface: a Photo-Renewable ¨Silver-Ions Electrode¨ for Neurotransmitters Detection

17:40 to 19:00

Poster presentation session and Wine tasting

New Materials

Room : Szent-Gyorgyi Albert Terem

Chaired by: Jan Macak

16:20 to 16:40

Pierre Millet (Chemistry, Paris-Saclay University, Orsay, France), Manuel Antuch, Akihiko Kudo, Angel Villagra

Photochemical Water Dissociation using Rh-doped $SrTiO_3$ Surface-modified by Pt-nanoparticles or Cobalt-clathrochelate Co-catalysts

16:40 to 17:00

Rochan Sinha (Electrochemical Materials and Interfaces, Dutch Institute for Fundamental Energy Research, Eindhoven, Netherlands), Anja Bieberle-Hütter, Bert Koopmans, Reinoud Lavrijsen, Irem Tanyeli, M.C.M. Van de Sanden

Electrochemistry of High Ion Flux Helium Plasma-exposed Iron Oxide Thin Films

17:00 to 17:20

Chun-Pei Cho (Applied Materials and Optoelectronic Engineering, National Chi Nan University, Nantou County, Taiwan), Fu-Jye Sheu

Graphene oxide-TiO_2-Ag_3PO_4 ternary composites with efficient photocatalytic performance for dye degradation and hydrogen evolution

17:20 to 17:40

Stéphane Bastide (Chimie Métallurgique des Terres Rares (CMTR), Institut de Chimie et des Materiaux Paris-Est (ICMPE), Thiais, France), Christine Cachet-Vivier, Taha El Assimi, Mathieu Halbwax, Joseph Harari, Raphael Lachaume, Sylvain Le Gall, Vincent Magnin, Encarnación Torralba Peñalver, Jean Pierre Vilcot

Microstructuration of Silicon Surfaces Using Nanoporous Gold Electrodes

17:40 to 19:00

Poster presentation session and Wine tasting

Tuesday 25 April 2017 - Morning

Keynote

Room : Juhasz Gyula Terem

Chaired by: Prashant Kamat

08:20 to 09:15 Keynote

Nathan S. Lewis (Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, USA)

Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting

Solar Fuels

Room : Juhasz Gyula Terem

Chaired by: Wolfram Jaegermann and Andrés G. Muñoz

09:20 to 10:00 Invited

Hyunwoong Park (School of Energy Engineering, Kyungpook National University, Daegu, Korea), Dong Suk Han, Unseock Kang, Jae-Joon Lee

All-Inorganic Solar Synthesis of Liquid Formate from CO_2 and Water over a Month on Durable and Recyclable Copper Iron Photocatalyst Films at Efficiency Exceeding Photosynthesis

10:00 to 10:20

Simon Filser (Nonequilibrium Chemical Physics, Technical University Munich, Garching, Germany), Katharina Krischer, Qi Li, Paolo Lugli, Thomas L. Maier, Robin Nagel, Werner Schindler, Tianyue Zhang, Josef Zimmermann

Photoelectrochemical CO_2 reduction at nanostructured gold/copper structures on Silicon

10:20 to 10:40

Micheal D. Scanlon (Chemical Sciences, Bernal Institute, University of Limerick, Limerick, Ireland), Andrés F. Molina Osorio

Unprecedented Levels of Electrochemical Control over Photosensitizer Assembly at Soft Interfaces to Achieve Solar fuels without Solid Electrodes

10:40 to 11:00

Coffee Break

11:00 to 11:20

Katharina Brinkert (TEC-SF, Noordwijk, Netherlands), Oemer Akay, Yasuhiro Fukunaka, Michael Giersig, Hans-Joachim Lewerenz, Janine Liedtke, Hisayoshi Matsushima, Slobodan Mitrovic, Matthias H. Richter

Photoelectrocatalysis: Solar-assisted Hydrogen Production in Microgravity Environments

11:20 to 11:40

Aldona Jelinska (Lab for Photoelectrochemistry and Solar Energy Conversion, Centre of New Technologies, University of Warsaw, Warsaw, Poland), Jan Augustynski, Krzysztof Bienkowski, Marcin Pisarek, Renata Solarska

Enhanced water splitting using tungsten trioxide-based photoanodes

11:40 to 12:00

Taek Dong Chung (Chemistry, Seoul National University, Seoul, Korea), Soo Youn Lee, Seong Yul Lim

Mask-Free Pattern for Solar Water Splitting and Biohybrid Electrode for CO_2 Reduction

12:00 to 12:20

Gabriel Loget (Institut des Sciences Chimiques de Rennes, CNRS, Rennes, France), Maissa Barr, Maimouna Diouf, Bruno Fabre, Francis Gouttefangeas, Loic Joanny, Lionel Santinacci

Electrochemically Structured Black Silicon for Water Oxidation

New Materials

Room : Szent-Gyorgyi Albert Terem

Chaired by: Pierre Millet and A. Wouter Maijenburg

09:20 to 10:00 Invited

Lionel Vayssieres (International Research Center for Renewable Energy, Xian Jiaotong University, Xian, China)

Dimensional, Interfacial, and Confinement Effects on the Performance and Stability of Low-Cost Photoelectrodes for Solar Water Splitting

10:00 to 10:20

Olga Krysiak (Lab for Photoelectrochemistry and Solar Energy Conversion, Centre of New Technologies, University of Warsaw, Warsaw, Poland), Jan Augustynski, Piotr Barczuk, Krzysztof Bienkowski

Plasmonic gold nanoparticles in Au/TiO_2 photocatalysts

10:20 to 10:40

Andrea Vezzoli (Chemistry, University of Liverpool, Liverpool, United Kingdom), Richard J. Brooke, Carly Brooke, Nicolò Ferri, Simon J. Higgins, Richard J. Nichols, Walther Schwarzacher

Molecular photoelectronics in Au/molecule/GaAs junctions

10:40 to 11:00

Coffee Break

11:00 to 11:20

Hyunjung Shin (Energy Science, Sungkyunkwan University, Suwon, Korea)

Atomic Layer Deposition of MoS_2 on Self-Supported Cu Substrate as Efficient Catalysts for Hydrogen Evolution

11:20 to 11:40

Dorottya Hursán (Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary), Csaba Janáky, Tamás Kiss, Attila Kormányos, Robert Ondok

Photoelectrochemistry of organic semiconducting polymers: fundamentals and implications in solar fuels generation

11:40 to 12:00

Julieth Suesca Botia (Faculty of Science, Universidad Industrial de Santander, Bucaramanga, Colombia)

Nitrogen and boron co-doped TiO_2 nanotubes (NB-NTTiO_2/Ti) with photoelectrochemical activity for paracetamol degradation in water using visible light

12:00 to 12:20

Vanousheh Rahemi (AXES, Chemistry, University of Antwerp, Antwerpen, Belgium), Willemien Anaf, Karolien De Wael, Koen Janssens, Dirk Lamoen, Bart Partoens, Nasrin Sarmadian

Unique Opto-Electronic Structure and Photo Reduction Properties of Sulfur Doped Lead Chromates Explaining their Instability in Paintings

Tuesday 25 April 2017 - Afternoon

Afternoon Visits

Optional Visits to either:

A)
Visit to Extreme Light Infrastructure - Attosecond Light Pulses ELI-ALPS facility only

B)
Visit to Extreme Light Infrastructure - Attosecond Light Pulses ELI-ALPS facility + sightseeing tour in Szeged

C)
Visit to Ópusztaszer (Hungarian National Heritage Park). Accompanying persons are also welcome. The additional costs for this visit amount to € 30 per person.

How to sign up: If you wish to participate at either of the above visits, please announce yourself upon registration on Sunday 23 April as from 14:00 until Monday 10:00 in the Hunguest Hotel Forrás. Groups will be allocated accordingly.
Every option will end at the restaurant where the banquet will be held.

Banquet

19:00-22:30
Fehértói Halászcsárda
Budapesti út 41, 6728 Szeged

Price for accompanying person : €45.
Transportation back to Hunguest Hotel Forras will be provided

Wednesday 26 April 2017 - Morning

Keynote

Room : Juhasz Gyula Terem

Chaired by: Gerko Oskam

08:20 to 09:15 Keynote

Laurence M. Peter (Department of Chemistry, University of Bath, Bath, United Kingdom)

Light-Driven Water Splitting: Achieving a Deeper Understanding

New Materials

Room : Szent-Gyorgyi Albert Terem

Chaired by: Lionel Vayssieres and Csaba Visy

09:20 to 10:00 Invited

Wolfram Jaegermann (Surface Science Division, TU Darmstadt, Darmstadt, Germany)

Solar fuels from artificial inorganic leafs - Physical boundary conditions and material science challenges

10:00 to 10:20

Thibaut Stoll (Solar Fuels, DIFFER, Eindhoven, Netherlands), Han Genuit, Bert Koopmans, Reinoud Lavrijsen, Michail Tsampas, George Zafeiropoulos

Innovative photoelectrochemical cells based on polymeric membrane electrolytes and suitable porous photoanodes

10:20 to 10:40

Giovanni Valenti (Department of Chemistry, University of Bologna, Bologna, Italy), Marcella Bonchio, Alessandro Boni, Paolo Fornasiero, Massimo Marcaccio, Michele Melchionna, Francesco Paolucci, Maurizio Prato, Stefania Rapino

Co-axial nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide

10:40 to 11:00

Coffee Break

11:00 to 11:20

Andrés Gualdrón-Reyes (Chemistry, Universidad Industrial de Santander, Bucaramanga, Colombia), Martha Niño-Gómez, Johan Rios-Niño

Influence of Cd/Mn Ratio on the Photoelectrochemical Properties of $Cd_{1-x}Mn_xS/Bi_2S_3$ Co-Sensitized Boron-Doped TiO_2 Nanotubes

11:20 to 11:40

Balázs Buchholcz (Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary), Tamás Boldizsár, Henrik Haspel, Zoltán Kónya, Akos Kukovecz

pH-regulated Antimony Oxychloride Nanoparticle Formation on Titanium Oxide Nanostructures: A Photocatalytically Active Heterojunction

11:40 to 12:00

Alireza Z. Moshfegh (Department of Physics & Nano Institute, Sharif University of Technology, Tehran, Iran (Islamic Republic of)), Mahdi Ebrahimi, orasae Samadi, Samira Yousefzadeh

Hierarchical ZnO nanostructures engineering: influence of surface morphology on photocatalytic and photoelectrochemical performance

12:00 to 12:20

Mitsuharu Chisaka (Department of Sustainable Energy, Hirosaki University, Hirosaki, Japan), Noriaki Itagaki, Yusuke Yamamoto

Support-Free-Titanium Oxynitride Nanocatalysts for Oxygen Reduction Reaction in Acidic Media

Novel Characterization Tools

Room : Juhasz Gyula Terem

Chaired by: Tamas Pajkossy and Maria Valnice Boldrin Zanoni

09:20 to 10:00 Invited

Gerko Oskam (Department of Applied Physics, CINVESTAV-IPN, Merida, Mexico), Rodrigo Garcia Rodriguez, Geonel Rodriguez Gattorno, Ingrid Rodriguez Gutierrez

Photoelectrochemical Characterization of Metal Oxides for Solar Water Splitting

10:00 to 10:20

Michelle Weber (Institute for Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Tuebingen, Germany), Marcus Scheele

Revealing Electronic Coupling in Semiconductor Nanoparticle Networks by Electrochemistry

10:20 to 10:40

Andrés F. Molina Osorio (Chemical Sciences, The Bernal Institute, University of Limerick, Limerick, Ireland), Micheal D. Scanlon

Dynamic Photoelectrochemical Analysis of Photo-induced Electron Transfer at the Interface between Two Immiscible Electrolyte Solutions Functionalized with Photocatalytic Porphyrin Aggregates

10:40 to 11:00

Coffee Break

11:00 to 11:20

Alexandre Baccaro (Fundamental Chemistry, University of Sao Paulo, Sao Paulo, Brazil), Lúcio Angnes, Ivano G.R. Gutz

The role of supporting electrolyte in the kinetic of photocatalytic processes: using the electrochemical approach for probing its effect on reactions at the interface of nanoparticulate P25 TiO_2

11:20 to 11:40

Damián Monllor-Satoca (Analytical and Applied Chemistry, Institut Químic de Sarrià, Universitat Ramon Llull, Barcelona, Spain), Teresa Andreu, Cristian Fàbrega, Joan Ramon Morante, Sebastián Murcia-López

Photocurrent Transients Revisited: Analysis of the Light-mediated Processes with a Wavelength-dependent Kinetic Model

11:40 to 12:00

Tamás Pajkossy (Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, HAS, Budapest, Hungary)

On the nature of the electrochemical double layer

12:00 to 12:20

Franziska Hegner (Chemistry, Institute of Chemical Research of Catalonia (ICIQ), Tarragona, Spain), Jose-Ramon Galan Mascaros, Sixto Gimenez, Nuria Lopez

Experimental and theoretical investigation of Prussian blue type redox catalysts for artificial photosynthesis

Poster Presentations

Poster presentation session and Wine tasting
on Monday 17:40 to 18:40

Poster presentation session
on Tuesnday 13:00 to 14:00

Solar Fuels

s1-001

Suresh Kannan Balasingam (Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway), Kaushik Jayasayee, Thirugnasambandam Manivasagam, Solon Oikonomopoulos, Svein Sunde, Srinivas Thangavel

Hematite/Graphene Bi-layered Photoelectrodes for Efficient Solar Fuel Conversion

s1-002

Gabriel Loget (CNRS / ISCR, Université de Rennes 1, Rennes, France)

Silicon Photoanodes Stabilized by Electrodeposited Ni Nanoparticles

s1-003

Yosohiro Sugie (Unit Team, Yumex Inc., Himeji, Japan), Yoshitaka Chigi, Kiyohiro Inoue, Sunao Ioku, Hiroki Sugishita

Development of Metallic Bipolar Plate for PEFC by Coating CarbonThin Film on Stainless Steel

s1-004

Lishan Zheng (Department of Gemology, University of Geosciences, Wuhan, China), Ting Lei, Chengbo Wang, Xinqiang Yuan

Influence of pulse period of PR plating on the properties of electrodeposited coatings of gold

Synthesis of Semiconductor Electrodes

s2-001

Fadi Kamal Aldibaja (Chemistry, ULB, Bruxelles, Belgium), Moussa Bougouma, Claudine Buess-Herman, Thomas Doneux, El Amine Mernissi Cherigui

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Light-Driven Water Splitting: achieving a deeper understanding

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The foundations of modern electrochemistry were laid by the parallel study of the electrical double layer and of electrode kinetics. I was delighted recently to find that Paul Delahay's 1965 classic *Double Layer and Electrode Kinetics* is still available on Amazon. It is a book that first inspired my interest in electrode kinetics, and it remains one of the most elegant and detailed treatments of the subject. This was the age of mercury. Clean perfectly smooth surfaces could be produced easily and reproducibly, giving access to reliable kinetic data. The problem of course is that no practical electrochemical devices such as batteries or fuel cells can be developed based on mercury. In the real world, we are confronted with solid electrodes and all the problems of irreproducibility that they bring (it was the late John Albery, I believe, who coined the helpful concept of the "reproducibly dirty electrode").

In the context of light-driven water splitting, we are interested in semiconductor electrodes. These bring added complications because the methods that are commonly used to study electrode kinetics on metal electrodes are generally not applicable to light-driven reactions at semiconductor electrodes. Techniques developed for metal electrodes rely on the fact that the activation energy for the electron transfer process (and hence the heterogeneous rate constant) can be changed by altering the potential drop across the double layer. However, the potential distribution across the semiconductor/electrolyte interface is more complex because a significant potential drop occurs in the semiconductor under depletion conditions. Furthermore, the electrode reactions of interest generally involve minority carriers, i.e. holes for n-type material and electrons for p-type materials. In the ideal case of low-doped semiconductors without surface states, we expect the rate constants for simple one step outer sphere electron transfer reactions involving minority carriers to be almost insensitive to applied potential because most of the potential drop occurs in the space charge region of the solid. However, the real-world situation is likely to be far from ideal in the case of water splitting photoelectrodes, since the reactions involve multistep electron transfer with adsorbed intermediates.

Given these difficulties, it is not surprising that no comprehensive treatment of photoelectrochemical electrode kinetics is currently available. Such a theory requires description of carrier generation/transport/recombination in the photoelectrode coupled to a detailed microscopic description of electron transfer and recombination at the interface. The theory will need to consider the mechanisms of multistep reactions and the roles of intermediates both in the overall reaction and, equally importantly, in surface recombination processes. In addition, the influence of surface intermediates on the potential distribution across the semiconductor/electrode junction needs to be accounted for. Finally, extension of any theory to nanostructured electrodes involves further levels of complexity.

The wide range of experimental methods used to study electrode kinetics at metal electrodes is mirrored in related techniques to study photoelectrochemical kinetics. The trick is to replace potential as the variable by light intensity. The light intensity controls the rate of generation of minority carriers, so we can, for example, suddenly initiate a flux of minority carriers towards the surface. Or we can modulate the flux sinusoidally. Or we can create a delta pulse of carriers. I will look at some of these methods in the talk. In these cases, we are not changing the rate *constants* if the photoelectrode is 'ideal'. Instead, we perturb the concertation of minority carriers at the surface and hence the *rate* (not rate constant) of the photoelectrochemical reaction. Remarkably, there are very few reported measurements of the rate constants for water splitting reactions. Often conclusions are drawn about 'catalysis' without any evidence that the rate constant for photoelectrochemical electron transfer has indeed been increased, rather than the rate constant for surface recombination decreased. Nevertheless, the few measurements that have been made have shown that the reactions involved in water splitting are remarkably slow, and the surface concentration of intermediates can be high, leading to problems with surface recombination.

Further information about mechanisms and kinetics can be obtained using non-electrical techniques such as in-situ spectroscopies, microwave reflectance methods and surface science studies. However, the desire to develop "champion electrodes" means that systems are often complex and difficult to model. We need more fundamental studies on well-defined systems as well as new theories describing the complex reactions involved in water splitting. I conclude that there is a great opportunity for experimentalists and theoreticians to achieve a deeper understanding of photoelectrochemical kinetics.

Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting

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We are developing an artificial photosynthetic system that will utilizes sunlight and water as the inputs and produce hydrogen and oxygen as the outputs. We are taking a modular, parallel development approach in which three distinct primary components-the photoanode, the photocathode, and the product-separating but ion-conducting membrane-are fabricated and optimized separately before assembly into a complete water-splitting system. The design principles incorporate two separate, photosensitive semiconductor/liquid junctions that will collectively generate the 1.7-1.9 V at open circuit necessary to support both the oxidation of H_2O (or OH^-) and the reduction of H^+ (or H_2O). The photoanode and photocathode will consist of rod-like semiconductor components, with attached heterogeneous multi-electron transfer catalysts, which are needed to drive the oxidation or reduction reactions at low overpotentials. The high aspect-ratio semiconductor rod electrode architecture allows for the use of low cost, earth abundant materials without sacrificing energy conversion efficiency due to the orthogonalization of light absorption and charge-carrier collection. Additionally, the high surface-area design of the rod-based semiconductor array electrode inherently lowers the flux of charge carriers over the rod array surface relative to the projected geometric surface of the photoelectrode, thus lowering the photocurrent density at the solid/liquid junction and thereby relaxing the demands on the activity (and cost) of any electrocatalysts. A flexible composite polymer film will allow for electron and ion conduction between the photoanode and photocathode while simultaneously preventing mixing of the gaseous products. Separate polymeric materials will be used to make electrical contact between the anode and cathode, and also to provide structural support. Interspersed patches of an ion conducting polymer will maintain charge balance between the two half-cells.

Rhodium-doped Titania: The Effect of the Doping Conditions on Bands Position and Density of Introduced Electronic States

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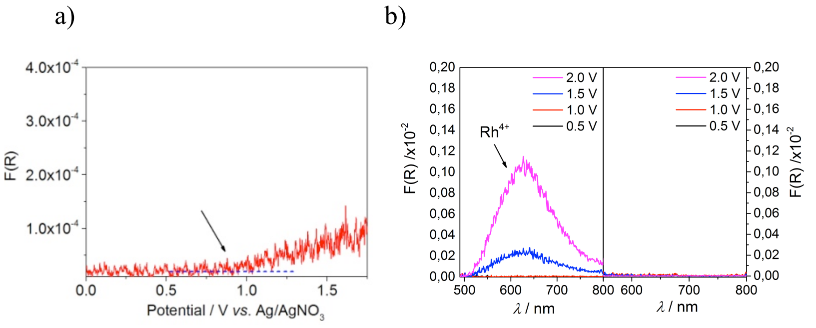
Doping of titanium dioxide with Rh ions improves significantly its activity under visible light.[1-4] Recently it was found, that in the case of rutile-based Rh-TiO_2 materials with low Rh-concentration (below 0.5mol.%) the photosensitization mechanism is based on two-step bandgap excitation of titania.[1, 2] Such a mechanism involves Rh^{3+} and Rh^{4+} species acting as built-in redox mediators and leads to generation of both: electrons in the conduction band and positive holes in the valence band of titania under irradiation with visible light (Fig. 1 c). Interestingly, such a process cannot be observed neither in the case of the samples containing more than 1mol.% of Rh nor for anatase-based materials prepared under the same conditions, in which Rh-species differently interact with titania lattice. The observed differences may be explained by the influence of various conditions of doping process (especially concentration of Rh species, crystalline structure of host material and preparation methods) on the electronic structure of the host material.

In the present studies spectroelectrochemical, photoelectrochemical and electrochemical measurements have been used for the estimation of density of the introduced states and determination of the influence of doping process on electronic structure of titania (Fig. 1 a, b). The obtained results, supported by spectroscopic measurements and photocatalytic tests, allowed to confirm the photosensitization mechanism (Fig. 1 c) and determine the dependency of observed properties on concentration of Rh ions and crystalline structure of titania. The obtained results as well as the attempts to use spectroelectrochemical and photoelectrochemical methods for the determination of the position of introduced electronic states within the bandgap of host semiconductor in other doped materials (e.g. Ir-doped titania) will be presented and discussed.



c)

Fig. 1. Changes of KM function at 625 nm with the applied potential recorded for 0.5% Rh-TiO_2 (a). Reflectance spectra in the representation of KM function recorded for 0.5% Rh-TiO_2 (left) and bare TiO_2 (right) at the various applied potentials (E *vs.* Ag/$AgNO_3$) (b). The measurements were carried out in deoxygenated 0.1 mol dm^{-3} $LiClO_4$ solution in acetonitrile. Scheme of the bands structure on the scale of potentials and possible light-induced electron transfer processes presented for Rh-TiO_2 (c).

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References

[1] J. Kuncewicz, B. Ohtani, *Chem. Comm.*, **2015**, *51*, 298- 301
[2] J. Kuncewicz, B. Ohtani, *RSC Advances*, **2016**, 6 77201-77211
[3] R. Niishiro, et al., *J. Phys. Chem. C*, **2007**, *111*, 17420- 17426
[4] W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.*, **1994**, *98*, 13669- 13679

TiO_2 Photocatalysis and Diamond Electrode

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The tremendous amount of research that has been carried out in the two closely related fields of semiconductor photoelectrochemistry and photocatalysis during the past three decades continues to provide fundamental insights and practical applications. The principles and measurements obtained TiO_2 with photoelectrochemical studies have led to the research activity on heterogeneous photocatalysis, where the strong photooxidative activity of TiO_2 has been applied to environmental cleanup. This resulted in the concept of “light cleaning”, i.e., deodorizing, disinfection, and decontamination of air, water and surface with TiO_2 thin films and light. In 1997, we reported the novel photo-induced superhydrophilicity of TiO_2 and proposed the concept of self-cleaning superhydrophilic properties of TiO_2.

We have the research center in our Noda Campus of Tokyo University of Science, named “Photocatalysis International Research Center”. In this center, we have three research groups, Artificial photosynthesis group (Demonstration experiment using sun light), Self-cleaning group (Performance evaluation using windows and walls), and Environmental cleanup group (Environmental cleanup with composite photocatalyst). Now we have three more research projects of Plant factory PJ, Liquid light-tube PJ and CO_2 reduction using diamond electrode PJ. In this meeting, I will explain and introduce the recent progress and our main targets of this research center.

Perovskite Solar Cells. Intricacies of Light Induced Processes

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With the emergence of highly efficient lead halide perovskites there is a need to understand the excited state behavior and charge separation events following photoexcitation. Mixed halide lead perovskites offer a useful strategy for continuous tuning of the semiconductor bandgap. For example, by varying the halide composition of methylammonium lead iodide/bromide ($CH_3NH_3PbBr_xI_{3-x}$ (x=0 to 3)) it is possible to tune the bandgap between 1.55 eV and 2.43 eV. In addition to photovoltaic applications these mixed halide perovskites offer rich photophysical properties with lasing applications. The excited state characterization using emission and transient absorption spectroscopy has allowed us to probe the photoinduced processes. Of particular interest are mixed halide lead perovskites (e.g.,$CH_3NH_3PbI_{3-x}Br_x$) which offer flexibility of tuning bandgap. Interestingly, they also undergo phase segregation to create Iodine-rich and Bromide- rich regions when subjected to visible irradiation. This intriguing aspect of halide ion movement in these mixed halide films can be tracked from the changes in the photoluminescence and absorption spectra. The photovoltaic performance of perovskite solar cells with varying degree of halide treatment will also be discussed

Effect of water content in electrolyte on anodic titanium oxide morphology and optical properties

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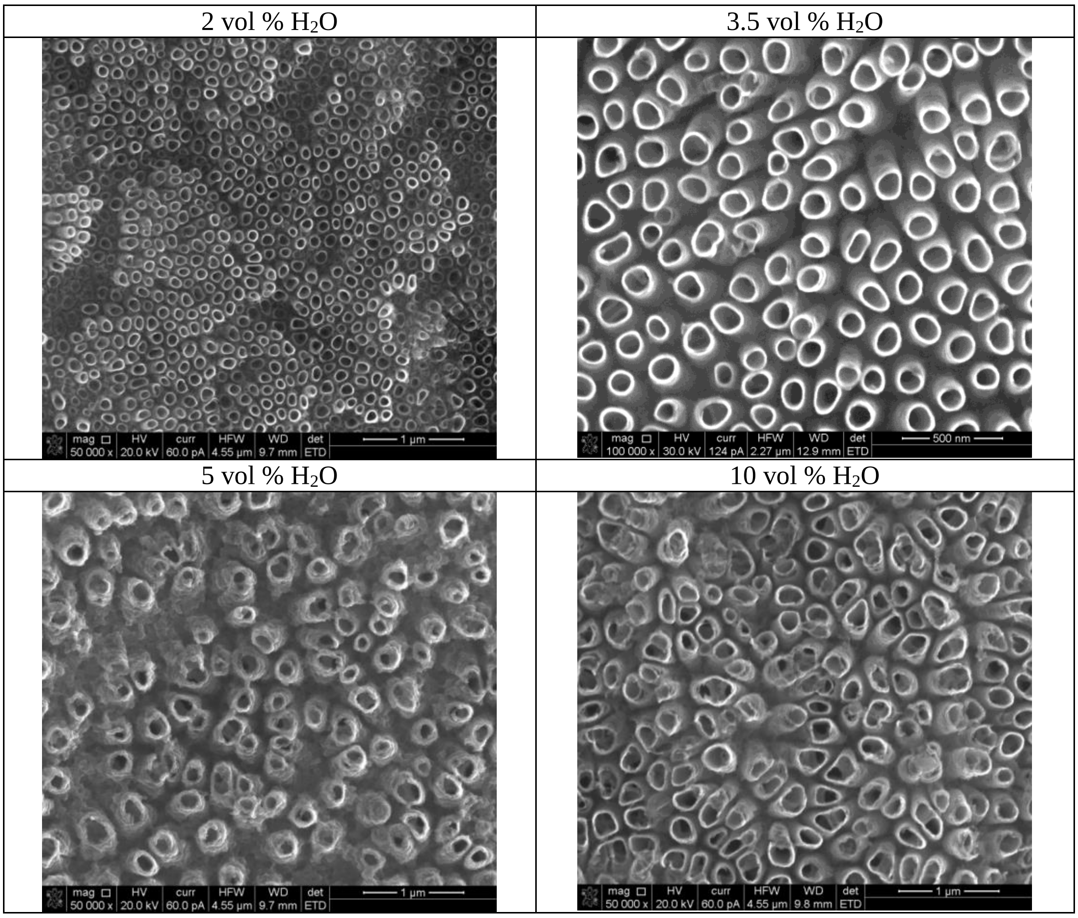
Morphology and optical properties of anodic titanium oxide (ATO) was investigated in details. Anodization was conducted in new ethanol-based electrolyte contained 0.3 M NH_4F and 2 – 10 vol% of water. It was found that the most ordered TiO_2 nanotubes arrays with relatively smooth walls were fabricated in electrolyte solution with 3.5 vol % water content. When the concentration of water in electrolyte was more than 3.5 vol % the inside diameter of oxide nanotubes increased but walls of ATO were destroyed. Moreover, it was shown that optical properties of received oxides were different depending of the electrolyte composition. Conditions to colored ATO formation was found. Presented method of colored TiO_2 fabrication could be applied to optical filters production.



2 vol % H_2O

3.5 vol % H_2O

5 vol % H_2O

10 vol % H_2O

Fig 1. ATO surface after anodization in ethanol-based electrolyte contain 0.3 M NH_4F and different water content.

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Boron-Doped Diamond Electrodes for Dye-Sensitized Solar Cells

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The generic semiconductor material in p-type dye-sensitized solar cells (p-DSCs; with sensitized photocathode) is p-NiO. An alternative semiconductor is B-doped diamond offering excellent chemical and electrochemically stability, optical transparency and favorable electrical properties. The electrochemical inertness of BDD is beneficial in view of the corrosive nature of certain electrolyte solutions used in DSCs. Spectral sensitization of BDD was carried out by anchoring of dyes like 4-(bis-{4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl}-amino)-benzoic acid (P1 from Dyenamo AB) with polyethyleneimine as a linker [1] or by covalent anchoring [2]. Alternative chemical modification of the diamond surface was performed through a combination of diazonium electrografting and Suzuki cross-coupling reactions [3]. The sensitized diamond exhibits stable cathodic photocurrents under visible light illumination in aqueous electrolyte solution with dimethylviologen serving as electron mediator [1-4]. The photoelectrochemical performance is similar or better compared to that of other sensitized diamond electrodes which were reported in previous studies [3]. To enhance the roughness factor for light harvesting, nanotextured BDD was prepared via silica templating route either by spherical templates [4] or electrospun nanofiber templates [5]. The material was tested for application with an aqueous electrolyte solution containing methyl viologen as a redox mediator. Cathodic photocurrents under solar light illumination (AM 1.5) are about 3-times larger on nanostructured electrodes compared to those on flat diamond, which was prepared with the standard chemical-vapor deposition (CVD). Illumination of the sensitized electrodes with chopped light at 1 sun intensity causes an increase of the cathodic photocurrent density to ca. 15-22 μA/cm^2. Photocurrent densities scale linearly with light intensity (between 0.1 a 1 sun), and they represent the largest values reported so far for dye-sensitized diamond electrodes. The photoelectrochemical activation of the sensitized diamond electrodes is accompanied with characteristic changes of the dark voltammogram of the MV^{2+}/MV^{+} redox couple and with gradual changes of the IPCE spectra. BDD electrodes also show interesting electrocatalytic activity (approaching that of platinum) in the classical DSCs with sensitized titania and Co-based redox mediators.

Acknowledgement: This work was supported by the Czech National Foundation, contract No. 13-31783S.

Reference List

[1] H. Krysova, Z. Vlckova-Zivcova, J. Barton, V. Petrak, M. Nesladek, M. Cigler, L. Kavan, Phys. Chem. Chem. Phys., 17 (2015) 1165.
[2] H. Krysova, J. Barton, V. Petrak, R. Jurok, M. Kuchar, P. Cigler, L. Kavan, Phys. Chem. Chem. Phys., 18 (2016) 16444.
[3] W. S. Yeap, D. Bevk, X. Liu, H. Krysova, A. Pasquarelli, D. Vanderzande, L. Lutsen, L. Kavan, M. Fahlman, W. Maes, K. Haenen, RSC Adv., 4 (2014) 42044.
[4] H. Krysova, L. Kavan, Z. Vlckova-Zivcova, W. S. Yeap, P. Verstappen, W. Maes, K. Haenen, F. Gao, C. E. Nebel, RSC Adv., 5 (2015) 81069.
[5] V. Petrak, Z. Vlckova-Zivcova, H. Krysova, O. Frank, A. Zukal, L. Klimsa, J. Kopecek, A. Taylor, L. Kavan, V. Mortet, Carbon, 114 (2017) 457.

Development of a Rapid, One-step Electrodeposition Method Resulting in Nanocrystalline TiO_2 Films with Enhanced (Photo)electrochemical Performance

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Several decades after the first reports on its properties, titanium-dioxide (TiO_2) is still one of the most intensively studied semiconductor. Because of its high photoactivity and (photo)chemical stability, it has been very frequently used in different fields, such as photocatalytic processes, photoelectrochemical water splitting, and dye-sensitized solar cells (DSSCs). During the years, many different synthetic protocols have been designed to obtain high-quality TiO_2: hydrothermal/solvothermal synthesis, the sol-gel method, and flame pyrolysis are all proper techniques to form TiO_2 with controllable particle size and morphology. To achieve proper crystallinity, however, high synthesis temperature must be applied. Moreover, for application as a thin film (e.g., in DSSCs), the formed nanoparticles have to be transferred to a proper substrate (e.g., via spray-coating), usually pursued by a several hours long sintering step. In summary, these methods are both time and energy consuming in nature, therefore there is a need for green and sustainable synthetic approaches.

In this study, we present a novel, one-step electrochemical method for the deposition of crystalline TiO_2 on different forms of carbon. $TiCl_3$ was employed as titanium source, and the TiO_2 was formed anodically by using a potentiostatic method. At a given solution composition, the key parameters of the synthesis were: (i) the pH of the solution, (ii) the applied potential (as suggested by the Pourbaix diagram of titanium), and (iii) the synthesis temperature. To deconvolute the complex effect of these parameters, a set of systematic experiments was carried out on glassy carbon electrodes. These studies included the investigation of (i) solution stability at various pH values, (ii) the effect of the deposition potential at a given pH, (iii) the effect of temperature on the crystallinity of the product. As we present here, by optimizing the circumstances, electrodeposition of an almost exclusively crystalline, porous TiO_2 layer can be achieved in a very short time (few minutes). We also note that via the presented method the phase composition can be controlled, and fine-tuned towards the targeted application, by simply varying the solution composition.

To demonstrate the robustness and general applicability of this synthetic approach, this method was extended to prepare TiO_2/3D-graphene hybrid photoelectrocatalysts. The conditions of the electrodeposition process were slightly modified and adjusted to this substrate, leading to the formation of a nanocrystalline material. Finally, the effect of the TiO_2-loading on the properties of the nanocomposite electrodes was evaluated by photoelectrochemical studies.

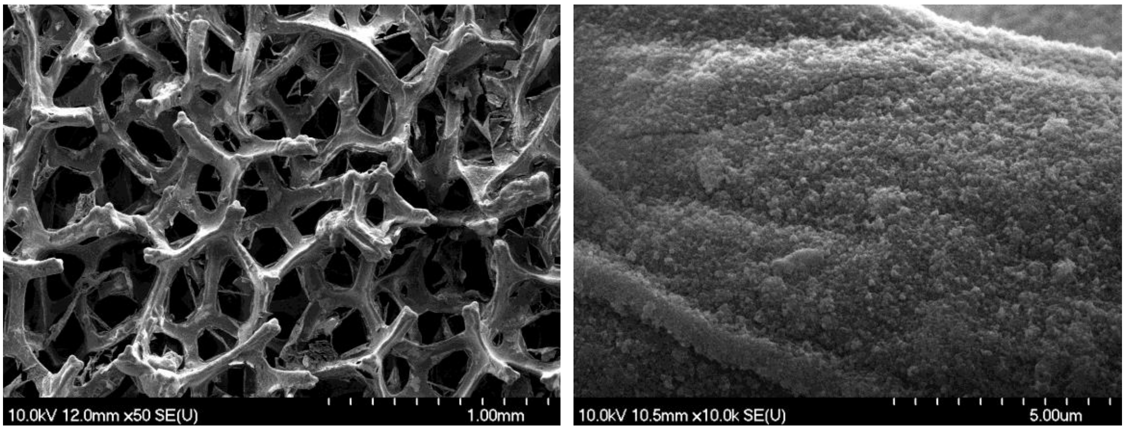

Figure 1. SEM images of a 3D-graphene/TiO_2 composite

Analysis and engineering of electronic states in semiconductor photocatalysts

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Heterogeneous photocatalysis is mostly based on the reduction and oxidation reactions taking place at the surface of illuminated semiconductors. Upon a photocatalyst excitation electrons and holes participating in these redox processes are generated. The energy of excited charges, and hence the feasibility of the redox processes, depends on the electronic structure of the photocatalyst, *i.e.* on the density of electronic states (DOS) localized close to the edges of valence and conduction bands. Experimental determination of DOS is therefore crucial for understanding the redox properties of semiconductors acting as photocatalysts and photoelectrocatalysts. Recently we developed a convenient spectroelectrochemical method of DOS determination (DRS-SEC), which combines electrochemical and spectroscopic measurements.[1,2] UV-vis spectral changes (recorded as DRS of the platinum electrode covered with the studied material) are analyzed as a function of the electrode potential. The measurements enable determination of the electronic states distribution and density close to the conduction band.

The DRS-SEC method has been successfully used to analyze the differences in photocatalytic activity of two crystalline forms of titanium dioxide – anatase and rutile (a-TiO_2, r-TiO_2).[3] So far, anatase was considered as a material characterized by a high photocatalytic activity in the processes of degradation of organic pollutants, while rutile remained virtually inactive in these processes. The mixture of a,r-TiO_2 is more active than any of these forms used separately. A unique photoactivity of a,r-TiO_2 is usually attributed to an efficient separation of charges in such composites. The DRS-SEC method allowed us to compare redox properties of a-TiO_2, r-TiO_2 and a,r-TiO_2. The results clearly showed that the lower edge of the conduction band, as well as available electronic states beneath it, are characterized by a potential *ca.* 0.5 V lower in the case of r-TiO_2 compared to a-TiO_2. It means that the excited r-TiO_2 material is a stronger reducer than a-TiO_2. A significantly better adsorption of oxygen at the surface of r-TiO_2 combined with very good reductive properties of this material make the reduction of oxygen to superoxide very efficient. It turns out that r-TiO_2 is also more active than a-TiO_2 in CO_2 reduction processes, some reactions of partial oxidation of organic compounds (*e.g.* oxidation of alcohols to aldehydes), as well as in the process of singlet oxygen generation formed as the result of $O_2^{\bullet-}$ oxidation with holes. This not only explains differences between anatase and rutile photoactivity, but allows for a more conscious design of photocatalysts.

The control of DOS distribution by means of chemical and structural modifications of a photocatalyst is feasible. The synthesis of photocatalysts (for CO_2 reduction and reactive oxygen species generation) with controlled distribution of electronic states within their band gaps will be presented. The application of DRS-SEC for determination of redox properties of selected groups of photocatalysts, as well as correlation between photocatalytic activity of the materials and their DOS characteristics, will be shown and discussed.

Acknowledgements

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References

[1] E. Świętek, K. Pilarczyk, J. Derdzińska, K. Szaciłowski, W. Macyk, *PCCP* **2013**, *15*, 14256-14261.
[2] M. Kobielusz, K. Pilarczyk, E. Świętek, K. Szaciłowski, W. Macyk, submitted.
[3] M. Buchalska, M. Kobielusz, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, *ACS Catalysis* **2015**, *5*, 7424-7431.

pH-regulated Antimony Oxychloride Nanoparticle Formation on Titanium Oxide Nanostructures: A Photocatalytically Active Heterojunction

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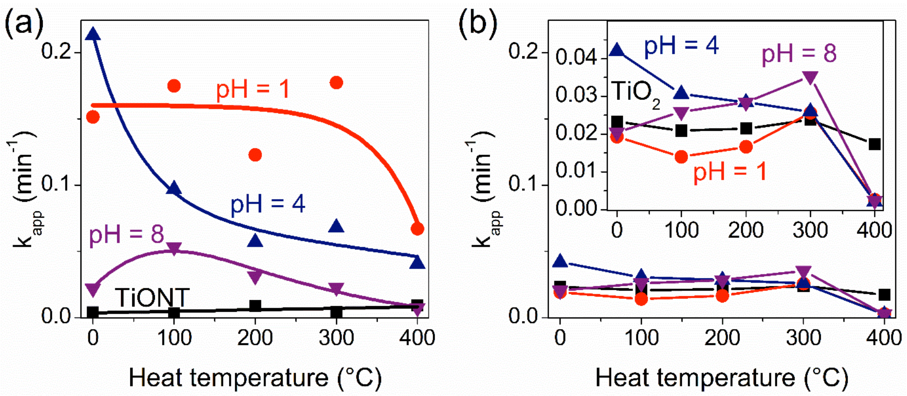
Improving the catalytic activity of heterogeneous photocatalysts has become a hot topic nowadays. To this end, considerable progress has been made in the efficient separation of photogenerated charge carriers by e.g. the realization of heterojunction photocatalysts. V-VI-VII compound semiconductors, namely bismuth-oxyhalides, are popular photocatalysts. However, results on antimony oxyhalides [$Sb_xO_yX_z$ (X = Br, Cl, I)], the very promising alternatives to the well-known $Bi_xO_yX_z$ photomodifiers, are scarce. Here, we report the successful decoration of titanium oxide nanostructures with 8-11 nm $Sb_xO_yX_z$ nanoparticles for the first time ever. Product size and stoichiometry could be controlled by the pH of the reactant mixture, while subsequent calcination could transform the structure of the used titanate nanotube support and the prepared antimony oxychloride. Even though $Sb_xO_yX_z$/TiONT composites formed easily, anatase TiO_2 could not facilitate the formation of antimony oxychloride nanoparticles on its surface. The resulting titanate nanotube-based composites showed photocatalytic activity in dye decolorization test reactions.



Variation of the apparent reaction rate constants in methyl orange decolorization with the calcination temperature in TiONT- (a), and TiO_2-based (b) $Sb_xO_yCl_z$ composites.

Photoelectrochemical Characterization of Metal Oxides for Solar Water Splitting

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Photoelectrochemical methods are a powerful tool to study novel metal oxides for solar water splitting, however, the interpretation of results are complicated by the nanostructured and porous character of many of these materials. As a consequence, it is not always clear if classical semiconductor electrochemistry models can be used to describe the results. The dye-sensitized solar cell is an example of this situation with a nanostructured, mesoporous photoelectrode, in which screened, dispersive diffusive electron transport is in balance with recombination processes characterized by electron transfer to the solution. Although TiO_2 is a semiconductor, the system is assumed to have electronic properties that are dominated by the presence of traps, and a description in terms of a band bending as a function of voltage is not accurate. The main recombination process is a photoelectrochemical reduction reaction of the electron acceptor in the solution. It has been shown that the transport and recombination kinetics are a function of the nanomaterial's properties.

A similar situation can occur for metal oxide materials for the conversion of sunlight to fuels such as hydrogen (H_2). However, depending on the material´s properties, different transport and recombinatin models maybe valid, which makes it necessary to look at these processes in detail. For this purpose, small-signal modulation methods can be used, including electrochemical impedance spectroscopy (EIS) and intensity-modulated photo voltage or photocurrent spectroscopy (IMVS/IMPS).

In the solar fuels research project, we use a combinatorial technique to search for new metal oxide nanomaterials for solar water splitting. In addition, we use advanced (photo)electrochemical methods in order to study the fundamental processes taking place in promising nanomaterials. Recent work has shown interesting results for the p-type semiconductor $CuBi_2O_4$, and we have analyzed the hole transport and recombination properties using EIS and IMPS/IMVS. In addition, we are investigating water oxidation on n-type oxide materials electrodes, using a variety of techniques. In this presentation, we will address recent experimental results and their interpretation, highlighting the complex nature of the interpretation of results in these interesting systems.

THE INFLUENCE OF APPLIED VOLTAGE AND SOLUTION TEMPERATURE ON PHYSICAL PROPERTIES OF ELECTRODEPOSITED ZnO THIN FILMS

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Zinc oxide (ZnO)is a technological important semiconducting material because of its interesting electrical resistivity, transparency in the visible, high electrochemical stability, direct band gap (3.3 ev)and abundance in nature. The electrochemical deposition method to produce materials in thin film configurations, attract interest of material researchers because noticeable advances when compared to standard methods: low cost, large scale depositions, low temperaturas processing and easy control thickness. In this work, 1Zinc oxide thin films were electrodeposited on fluorine-doped tin oxide (SnO_2:F) deposited previously by chemicals spray substrates in an aqueous medium of zinc nitrate $Zn(NO_3)_2$ at 0.1M with a solution pH = 6. The electrodeposition cell employed a standard three electrode geometry comprising SnO_2 glass substrate with a sheet resistance of 10 ohm-cm a graphite rod and a saturated calomel electrode (SCE) as working, counter and reference electrodes, respectively. Before use, the tin conductive oxide substrates were treated for 5 min with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The films depositions were carried out sytematically:In a first round the temperture was kept fixed and the linear voltage was increased from 1250 to 1450 mV in 50 mV steps, then for an optimal voltage, temprature was rised from 25 to 85 ªC in 10 ªC steps. Deposition time was 30 minutes for all the cases.

XRD studies were carried out with a JEOL JDX 8030 diffractometer using CuK_a radiation. Optical transmission measurements were performed using a HP AGILENT UV-Vis spectrophotometer in order to evaluate the energy gap of the electrodeposited semiconductors. An SnO_2:F-covered glass substrate was placed in the reference optical path to compensate the light intensity. Scanning electron microscopy (SEM) images were obtained using a LV JEOL 5600 microscope at an acceleration voltage of 20 kV.

After finding the appropiate linear voltage for electrodeposition, ZnO Films were produced with polycrystalline characteristics.Films grown with parameters before mentioned look regular and compact when observed at low magnifications, but the surface configuration change in grain size distribution and in morphology from almost rounded shapes to flake-like first ant then to flower-like configuration. In some cases plate-like grains, appear with pile-up configuration which suggest some level of epitaxy during the growing process.These last details were corroborated when the samples were observed with atomic force microscopy in the contact mode.

The surface resistivity and electro-optical parameters were determine for each sample and were correlated when possible with the structural and morphological details derived from atomic force and scanning and transmisión electron microscopy observations

Solar fuels from artificial inorganic leafs – Physical boundary conditions and material science challenges

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One of the most demanding research aims for an holistic and sustainable energy economy is the integration of storage devices to solar energy converters to overcome the discontinuous supply of solar power. The direct production and use of chemical fuels would provide a favourable solution. However, inherent problems in the direct production of H_2 from solar light has not been solved yet in a satisfying way.

Direct H_2 formation by **photo electrochemical H_2O splitting** theoretically provides high light (photon) to fuel (H_2) efficiency. Advanced materials and design concepts based on the coupling of wide band gap semiconductors i.e. ZnTe, GaP, SiC or thin film Si or 3-5 tandem (multijunction) cells and nano sized metal catalysts are considered as very promising options. Alternatively band gap modified and defect engineered nanosized oxides are considered as alternatives to meet the requirements. Materials and devices of this type must be designed, grown, processed and characterized combining the demands of a photovoltaic converter coupled loss free to an efficient electrolyser component.

From a consideration of the given thermodynamic and kinetic conditions to split H_2O we expect that only tandem (multijunction) structures with a sufficient splitting of the quasi-Fermi level equivalent to the provided photovoltage of the solar converter component will be able to split H_2O into H_2 (HER) and O_2 (OER. As a consequence the first duty is to optimize the light converting devices structure in a similar way as it has to be done for electric power producing solar cells. This means that the transport lengths of charge carriers must exceed the thickness of the device, where the thickness of the absorber layer has to exceed the absorption length for planar systems. Subsequently the separated charge carriers must be transferred to the surface reaction sites without loss in chemical potentials (photovoltage) and loss in photocurrent. In the case of multi electron transfer reactions catalysed by metallic particles the interactions of intermediates of the HER and OER with the electro catalyst's surfaces must be taken into account. For minimizing loss mechanism the position of the band edges, metal Fermi level, and electrolyte density of states must be arranged in a proper way. We suggest that only buried junction devices will be able to fulfil these conditions.

We will present and discuss our research approach on photo electrochemical water splitting devices giving a survey on most interesting systems from our point of view. The materials science issues, which are needed to overcome often given limitations of H_2O splitting devices will be discussed and results of recent experimental investigations to verify our concepts will be presented. In collaboration with FZ Jülich triple thin film Si solar cells have been developed which has reached 9.5 % solar to H_2 efficiency. These devices are clearly defined examples of promising design concepts of further improved fuel producing solar converter cells.

Photoelectrochemical synthesis of conducting polymer/inorganic semiconductor assemblies

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In recent years much focus has been devoted to the synthesis of hybrid materials consisting of conducting polymers (CPs) and inorganic semiconductors. Great efforts are dedicated to develop new synthesis tools to prepare such complex systems, understand their working principles, and to expand the field of possible applications [1]. Currently such hybrids are often utilized in energy conversion and storage. In these areas the efficiency of charge carriers generation and transport dictate the final device performance, thus special emphasis is given on the quality of the interfaces between the constituents. In these application scenarios nanostructured electrodes offer several advantageous properties compared to their planar counterparts. Apart from their higher surface area they possess enhanced carrier lifetime, because charge transport involves less grain boundaries in these ordered systems. In the case of solar cell applications it is necessary to involve a third component to enhance light absorption and to promote charge transfer between the CP and the inorganic semiconductor. These so called sensitizers can be organic dyes, metal-chalcogenide quantum dots, and lately organic-inorganic hybrid perovskite compounds.

In our work, we apply a versatile method to fabricate such metal-oxide nanostructures; namely the electrochemical anodization of the respective metal foils (e.g., Ti, W, Nb) in the presence of a complexing agent (usually F^-). Through the deliberate variation of the anodization parameters (e.g., solution composition, applied bias, and water content) nanoporous or even nanotubular structures can be obtained, which maintain electric contact with the supporting electrode.

A multitude of synthetic techniques, ranging from simple physical to more sophisticated electrochemical and photoelectrochemical methods, are available for the deposition of the CP on the above assemblies. In the case of nanostructured scaffolds however, only a few of these are capable of maintaining the rigorous control over the quality of the forming interfaces. Furthermore, the complete filling of nanostructured electrodes by physical infiltration poses a difficulty because of mass transport limitations, arising from the diffusion of the large molecular weight polymers into the porous structures. Therefore it is necessary to employ more sophisticated electrochemical methods, where CPs are in situ generated in the pores of the nanostructures from their monomeric building blocks. These techniques can be further augmented by employing simultaneous light irradiation, thus exploiting the semiconductor nature of the components (both the oxide scaffold and any sensitizer anchored on it).

The main focus of this study is on the mechanistic aspects of the photoelectrochemical deposition technique of poly(3,4-ethylenedioxythiophene) on ordered TiO_2 nanotubes decorated with CdS or CdSe nanocrystals. The TiO_2 nanotube arrays were fabricated via anodization and were decorated with the Cd-chalcogenide nanocrystals with the SILAR (Successive Ionic Layer Adsorption and Reaction) method. The deposition of the CP was then carried out by photoelectrochemical techniques by employing collective or selective excitation of the TiO_2/Cd-chalcogenide scaffold [2]. We found that the most decisive parameter during the photoelectrodeposition is the wavelength distribution of the used illumination as well as the role of competing procedures in the solution and on the semiconductor/electrolyte interface.

[1] C. Janáky, K. Rajeshwar, Prog. Polym. Sci. 43 (2015) 96–135.
[2] G.F. Samu, C. Visy, K. Rajeshwar, S. Sarker, V.R. Subramanian, C. Janáky, Electrochim. Acta. 151 (2015) 467–476.

Photo-electrodeposition of Rhodium on III-V Semiconductors for the Construction of Tandem Water Splitting Devices

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Solar water splitting tandem devices are a promising route for building a carbon-neutral energy infrastructure based on hydrogen as a fuel (1). Recent developments in high-efficiency III-V photovoltaics suggest the use of these advanced material engineered concepts for their construction. A successful technical realization needs the coupling of fast electrochemical catalysis to these systems (two in one systems, figure 1) (2,3). This requires from smart conditioning methods to turn semiconductor surfaces both electrochemical active and chemically stable in contact with electrolyte. Particularly, the decoration of with noble metals, such as Pt and Rh is one of the most pursued approaches in the design of photocathodes to be integrated tandem-type devices (3). Electroplating is preferred method due to its simplicity, its low cost and its power for accessing hidden places in complicated geometrical shapes (structured surfaces). The optical and electrocatalytic performance of deposited metal film can be tuned by achieving a particular size and distribution of clusters. Chemical composition of bath, applied potential program and illumination intensity constitute the main tools to do this.

Electroplating of noble metals onto p-semiconductors, however, triggers interfacial reactions generating strong chemical and electronic surface transformations linked with side photo-elctrochemical reactions (4). This is due to the complex multi-electron transfer involved in the metal phase formation and the particular high thermodynamic redox potential. Therefore, the selection of a galvanic method must balance coupled interfacial processes with desired properties of the electrocatalytic film.

The complex picture of electrocrystallization of Rh will be discussed in the light of electrochemical experiments, surface and spectroscopic characterization (HR-TEM, Synchrotron XPS) experiments performed on silicon, InP and GaInP. These systems are characterized by the formation of an interfacial oxide film separating electrocatalytic particles from the absorbing semiconductor. The composition and electronic structure of this latter builds a particular energetic pathway chart that defines the electrode performance.

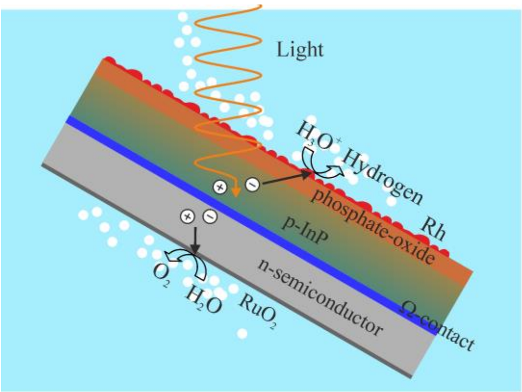

Figure 1: schematic of a typical tandem solar water splitting cell

1. Muñoz AG, Lewerenz HJ (2010) Advances in photoelectrocatalysis with nanotopographical photoelectrodes, ChemPhysChem 11:1603-1615
2. Döscher H, Supplie O, May MM, Sippel P, Heine C, Muñoz AG, Eichberger R, Lewerenz HJ, Hannappel T (2012) Epitaxial III-V films ans surfaces for photoelectrocatalysis, ChemPhysChem 13:2899-2909.
3. May M, Lewerenz HJ, Lackner D, Dimroth F, Hannappel T (2015) Efficient direct solar-to-hydrogen conversion by in situ interface transformation of a tandem structure, Nature Commun. 6:8286.
4. Muñoz AG, Heine C, Lublow M, Klemm HW, Szabó N, Hannappel T, Lewerenz HJ (2013) Photoelectrochemical conditioning of MOVPE p-InP films for light-induced hydrogen evolution: chemical, electronic and optical properties, J. Solid State Tech. 2: Q51-Q58.

Graphene oxide-TiO_2-Ag_3PO_4 ternary composites with efficient photocatalytic performance for dye degradation and hydrogen evolution

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Graphene oxide-enwrapped and TiO_2-decorated Ag_3PO_4 ternary composites with high optical response to visible light and good stability were fabricated by a facile and low-cost method. In the composites, the Ag_3PO_4 particles were of sphere-like shape and with micron size, and TiO_2 were anatase nanoparticles. Compared with other carbonaceous or TiO_2-containing binary composite photocatalysts, this kind of ternary composite has shown superior photocatalytic activities on dye degradation and hydrogen production from water splitting. Furthermore, they exhibited antibacterial capability. The presence of graphene oxide and Ag_3PO_4 in the ternary composites has been evidenced by XRD patterns, XPS analysis, Raman spectra and HRTEM microstructures, etc. Various molar ratios of Ag_3PO_4 and TiO_2 were employed during the fabrication processes to explore the impacts of the content of Ag_3PO_4 on photocatalytic efficiencies. From the results of electrochemical analysis, photodegradation and hydrogen evolution tests, it has been demonstrated that the optimum activities were achieved when the ratio of Ag_3PO_4 and TiO_2 was 0.6. The improved efficiencies could be attributed to the synergistic effects derived from the heterostructure formed by graphene oxide, TiO_2 and Ag_3PO_4. Radicals trapping experiments were also performed so as to elucidate the photocatalytic reaction mechanism.

Nitrogen and boron co-doped TiO_2 nanotubes (NB-NTTiO_2/Ti) with photoelectrochemical activity for paracetamol degradation in water using visible light.

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Spectroscopic techniques have allowed to identify in waste-water a new type of pollutants, which are of difficult degradation and have a high potential to generate negative effects on human health, flora and fauna; also, which have been recognized as emerging contaminants[1] [2]. The Paracetamol is an analgesic and antipyretic pharmaceutical product, it is considered one of the three medicaments more used by prescription and during the last years, in Colombia, one of the most common because of apparition of virus such as: Dengue, Chikungunya and Zyka, doing of this pharmaceutical product a contaminant of emerging concern.

The preparation of electrodes based on TiO_2 nanotubes and co-doped with nitrogen and boron (N, B/NT-TiO_2/Ti) is proposed as an alternative to extend absorption range of TiO_2 from UV region to other of less energy (visible region) and to improve photoanswer of co-doped TiO_2 nanotubes in comparison to TiO_2 nanotubes without doping (NT- TiO_2/Ti) or monodoped with nitrogen or boron separately and with photo-oxidation power to break down complex molecules, as paracetamol by photoelectrochemical processes.

Nitrogen and boron co-doped nanotubes (N, B/NT- TiO_2/Ti) were obtained by electrochemical anodization, using boric acid (H_3BO_3) and urea $CO(NH_2)_2$ as dopant precursors. The nanotubes were characterized by spectroscopic techniques such as: FESEM, XRD, DRS and XPS, while their photoelectrochemical properties were evaluated through measurements of open-circuit potential (OCP), Linear sweep voltammetry (LSV), cyclic sweep voltammetry (CV) and impedance spectroscopy, using a three electrodes cell, a graphite bar as counter-electrode, an electrode of Ag/AgCl (3 M KCl) as a reference electrode and the photoelectrodes of N, B/NT- TiO_2/Ti as working electrodes.

The activity of N, B/NT- TiO_2/Ti nanotubes was evaluated by photoelectrochemical degradation of a solution of paracetamol (20 mg/L) and Na_2SO_4 0.1 M using a conventional two-electrode cell. The reaction was monitored using Liquid Chromatography. The N, B/NT- TiO_2/Ti nanotubes a high activity during the photoelectrochemical oxidation of paracetamol, because there were obtained good percentages of degradation and complete mineralization of this compound. The photoelectrochemical process showed more efficiency to oxidation of paracetamol in comparison to photocatalysis, direct photolysis and electrochemical process.

References

1. X. Zeng, X. Guo, G. Su, M. K. Danquah, S. Zhang, Y. Lu, Y. Sun, and L. Lin, “Bioprocess considerations for microalgal-based wastewater treatment and biomass production,” Renewable Sustainable Energy Rev., vol. 42, pp. 1385–1392, 2015.

2. C. Siah, L. J. Robinson, y M. Fong Chong, “A review on application of flocculants in wastewater treatment,” Process Saf. Environ. Prot., vol. 92, pp. 489–508, 2014.

Photochemical Water Dissociation using Rh-doped $SrTiO_3$ Surface-modified by Pt-nanoparticles or Cobalt-clathrochelate Co-catalysts.

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Water is a source of carbon-free hydrogen, an energy vector of interest which can be produced from sunlight in view of the so-called "hydrogen economy". In the current state-of-art, a two step process is favored for close-to-ambient-temperature water dissociation: (i) the photon-to-electron conversion using a PV panel; (ii) the electron-to-chemical conversion using an electrolysis cell. Both steps can be combined for a direct photon-to-chemical conversion using either a photochemical or a photo-electrochemical reactor. While the conversion efficiency of the two-step process is now close to 25% [1], it is still significantly lower in the integrated devices and significant progress is needed in material science before applications can be developed. We report here on the kinetics of water photo-dissociation using strontium titanate as photo-active material, surface-modified by two different co-catalysts. Rhodium doping is used to modify the band structure of the perovskite and extend its light absorption range towards visible light [2]. Methanol is used as sacrificial agent in the experiments (the overall reaction under investigation is therefore the endergonic methanol steam photo-reforming reaction). Figure 1 shows the kinetics of hydrogen evolution at room temperature using Rh(1%)-$SrTiO_3$ without co-catalyst. This is the reference case, with and without a UV filter that cuts radiations with wavelength less than 400 nm. Figure 2 shows the kinetics of hydrogen formation at room temperature using Rh(1%)-$SrTiO_3$ with surface Pt nanoparticles (0.3wt.% Pt). The kinetics is significantly increased, by a factor of approximately 20, suggesting that the kinetics of the surface charge-transfer step might be rate-determining, or at least is playing a significant role in the overall kinetics. Then, we investigated the co-catalytic activity of transition metal-based molecular co-catalysts. Figure 3 shows a plot of the improvement factor Φ (a measure of the kinetics compared to the reference case) as a function of the concentration of bisfluoroboryltrisdimethyl glyoximato cobalt $[Co(III)(dmg)_3(BF)_2]BF_4$ in solution (a cobalt complex of known activity with regard to the hydrogen evolution reaction [3]). A co-catalytic effect (less than Pt) is put into evidence, with a maximum activity that corresponds to monolayer thick sorption isotherms.

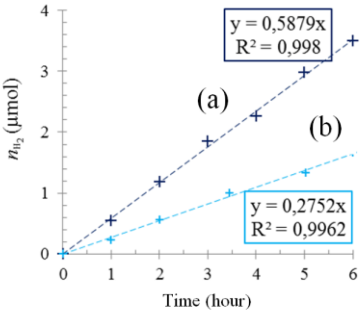

Fig. 1 : H_2 mole number evolved vs. time. 20 mg Rh(1%)-$SrTiO_3$ in water + 10 vol.% MeOH. (a) no UV filter; (b) UV filter.

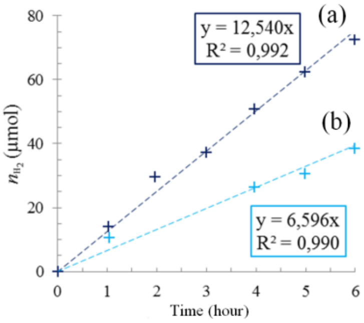

Fig. 2 : H_2 mole number evolved vs. time. 20 mg Rh(1%)-$SrTiO_3$-Pt(0.3%) in water + 10 vol.% MeOH. (a) no UV filter; (b) UV filter.

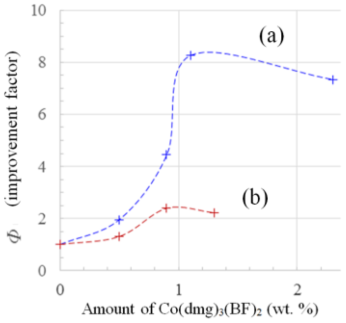

Fig. 3 : improvement factor Φ vs. Co-wt.% in solution. 20 mg Rh(1%)-$SrTiO_3$ in water+10 vol.% MeOH. (a) no UV filter; (b) UV filter.

References

[1] A. Nakamura, Y. Ota, K. Koike, Y. Hidaka, K. Nishioka, M. Sugiyama, K. Fujii, *A 24.4% solar to hydrogen energy conversion efficiency by combining concentrator photovoltaic modules and electrochemical cells*, Applied Physics Express 8 (2015) 107101.

[2] R. Konta, T. Ishii, H. Kato, A. Kudo, *Photocatalytic activities of noble metal ion doped $SrTiO_3$ under visible light irradiation*, J. Phys. Chem. B., Vol. 108, 2004, pp. 8992-8995.

[3] O. Pantani, S. Naskar, R. Guillot, P. Millet, E. Anxolabéhère, A. Aukauloo, *Cobalt Clathrochelate Complexes as Hydrogen-Producing Catalysts*, Angewandte Chemie Int. Ed. 120 (2008), 10096-10098.

Photocurrent Transients Revisited: Analysis of the Light-mediated Processes with a Wavelength-dependent Kinetic Model

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Incident Photon-to-Current Efficiency (IPCE) is a common and widely used measure of the efficiency of photoactive electrodes [1] that stems from the photocurrent as a function of wavelength (i.e. action spectra). Conventionally, the photocurrent values are taken upon a certain stabilization time, whereas the transient behavior is generally omitted in such action spectra. However, the transient photocurrent entails a large amount of mechanistic information regarding the charge generation, transport, recombination and interfacial transfer processes [2, 3], provided a proper and relatively simple model [4, 5] is used; in this contribution, we propose a straightforward and easy-to-implement photocurrent model by solving the charge transport equation upon the assumption that the light penetration varies with wavelength. For an n-type semiconductor film and in the presence of band bending, the normalized photocurrent transients eq. (1):

$$\frac{j(t,\lambda)-j_{ph}}{j_0-j_{ph}}=\exp\left[-\left(\frac{1}{\tau}-T(\alpha^{-1})\right)t\right] \tag{1}$$

where $j(t, \lambda)$ is the wavelength-dependent photocurrent density ($\mathrm{A\cdot cm^{-2}}$); j_0 and j_{ph} are its limiting values in the beginning and in the ending of the photocurrent transient, respectively; τ is the electron lifetime (s); and $T(\alpha^{-1})$ is a charge transport term that varies as a function of light penetration (α^{-1}). The model is illustrated with a range of modified and unmodified n-type metal oxides thin films.

[1] Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarsctein, A. J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E. W. McFarland, K. Domen, E. L. Miller, J. A. Turner, H. N. Dinh. *J. Mater. Res.* **2010**, *25*, 3-16.
[2] A. Hagfeldt, H. Lindström, S. Södergren, S-E. Lindquist. *J. Electroanal. Chem.* **1995**, *381*, 39-46.
[3] W. H. Leng, P. R. F. Barnes, M. Juozapavicius, B. C. O´Regan, J. R. Durrant. *J. Phys. Chem. Lett.* **2010**, *1*, 967-972.
[4] L. M. Abrantes and L. M. Peter. Transient photocurrents at passive iron electrodes. *J. Electroanal. Chem.* **1983**, *150*, 593-601.
[5] L. M. Peter, J. Li, R. Peat. Surface recombination at semiconductor electrodes. Part I. Transient and steady-state photocurrents. *J. Electroanal. Chem.* **1984**, *165*, 29-40.

Anodic oxidation as a simple and cost-effective method for fabrication of nanostructured semiconductor oxides with various morphologies

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Recently, semiconducting oxide nanostructures, such as nanowires, nanotubes or nanoporous layers, have been extensively investigated due to their unique properties, e.g. ultrahigh surface-to-volume ratio and higher charge carrier mobilities compared to the bulk materials. However, the main problem that limits the practical application of such nanomaterials is a relatively high cost of nanofabrication process. As a result, considerable research efforts worldwide focus on the design and control of novel nanostructures via innovative synthetic strategies. A variety of methods have been already employed for fabrication of nanostructured semiconductor oxides. Among them, simple anodic oxidation (anodization) of metallic substrate, widely recognized as an easy way to synthesize nanoporous alumina [1] and nanoporous or nanotubular titania [2] have been recently employed for fabrication of many nanostructured semiconducting oxides with various morphologies [3]. The aim of this presentation is to give an overview of some recent results on electrochemical fabrication and complex characterization of nanostructured semiconductor oxides such as nanoporous tin oxide (SnO_x) layers (see Figure 1A–C) [4,5], zinc oxide (ZnO) nanowires (see Figure 1 D, E) and nanoporous tungsten oxide (WO_3) films (see Figure 1F). A special emphasis will be put on some novel synthetic strategies allowing for fabrication of anodic films with precisely designed morphology as well as on photoelectrochemical activity of such kind of materials.

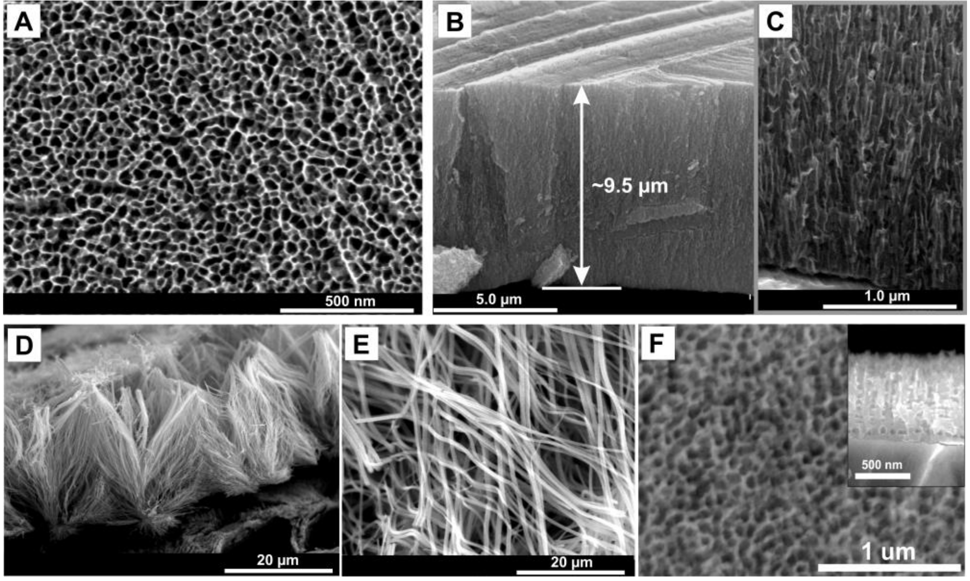

Figure 1. FE-SEM images of nanostructured oxides such as: porous SnO_x (A–C) , ZnO nanowires (D, E) and porous WO_3 (F) formed by anodic oxidation of metallic substrates under appropriate conditions.

Acknowledgement
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References

[1] L. Zaraska, A. Brudzisz, E. Wierzbicka, G.D. Sulka, Electrochim. Acta 198 (2016) 259–267.
[2] J. Kapusta-Kołodziej, L. Zaraska, G.D. Sulka, Appl. Surf. Sci. 315 (2014) 268–273.
[3] A. Ghicov, P. Schmuki, Chem. Commun. 2009, 2791–2808.
[4] L. Zaraska, K. Syrek, K. Hnida, M. Bobruk, A. Krzysik, T. Łojewski, M. Jaskuła, G.D. Sulka, Electrochim. Acta 205 (2016) 273–280.
[5] L. Zaraska, D. Gilek, K. Gawlak, M. Jaskuła, G.D. Sulka, Appl. Surf. Sci. 390 (2016) 31–37.

On the nature of the electrochemical double layer

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Since Helmholtz's statement in 1879, the double layer has been regarded to be capacitive, implying instantaneous double layer structure changes following those of voltage. Accordingly, the vast majority of the double layer theories in the past hundred years have been of static nature; time or frequency do not appear in the resulting equations. In other words, the kinetics of the double layer rearrangement processes have always been out of the scope.

Recent advances of methodology enabled precise studies of the kinetics of double layer rearrangement processes. To be presented are results of impedance spectroscopy measurements, made in cooperation with colleagues at the Ulm University in the past decade. These experiments have been performed with systems which are very simple and well-defined from conceptual points of view – like CV and EIS measurements on Pt(100) in aqueous HCl solutions or on Au(100) and HOPG in ionic liquids. The results demonstrate that charging-discharging of the double layer is far from being immeasurably fast; in particular, in the case of the ionic liquids these processes are rather sluggish. These demonstration experiments are aimed to urge theoreticians to include slow adsorption-desorption and local transport processes in their double layer models.

Though all the cases to be presented refer to noble metal | electrolyte systems, the basic idea – that the double layer reorganization processes are governed not by electrostatics only – *mutatis mutandis* applies also for semiconductor-electrolyte interfaces as well.

References:

1. T. Pajkossy, Impedance spectra of Pt(100) in aqueous H_2SO_4 and HCl solutions around the hydrogen adsorption-desorption peak, *Z. Phys.Chem*., **226** (2012) 935-943
2. C. Müller, K. Németh, S. Vesztergom, T. Pajkossy, and T. Jacob, The interface between HOPG and 1-butyl-3-methyl-imidazolium hexafluorophosphate, *Phys.Chem.Chem.Phys*., **18** (2016) 916-925

Hybrid and Functionalized Interfaces for Photoelectrochemical and Electrocatalytic Reduction of Carbon Dioxide

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There has been growing interest in the photoelectrochemical conversion of carbon dioxide (a potent greenhouse gas and a contributor to global climate change) to useful carbon-based fuels or chemicals. The reaction products are of potential importance to energy technology, food research, medical applications and fabrication of plastic materials. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. It is often postulated that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate. In this respect, the proton availability and its mobility at the photo(electro)chemical interface has to be addressed. On the other hand, competition between such parallel processes as hydrogen evolution and carbon dioxide reduction has also to be considered.

Recently, we have concentrated on the development of hybrid materials by utilizing combination of metal oxide semiconductors thus capable of effective photoelectrochemical reduction of carbon dioxide. For example, the combination of titanium (IV) oxide and copper (I) oxide has been considered before and after sunlight illumination. It is reasonable to expect that the light absorbed by the inner Cu_2O film produces energetic electron (e^-) – hole (h^+) pairs. The excited electrons are driven through the conduction band to the external TiO_2/electrolyte interface. The role of TiO_2 is not only stabilizing: the oxide is also expected to prevent the recombination of charge carriers (e^- - h^+ pairs). Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. Among important issue is intentional stabilization, activation, and functionalization of the mixed-metal-oxide-based photoelectrochemcal interface toward better long-term performance and selectivity production of small organic molecules (C1-C4) and other chemicals. In this respect, ultra-thin films of conducting polymers (simple or polyoxometallate-derivatized) and supramolecular complexes (with nitrogen containing ligands and certain transition metal sites), sub-monolayers of metals (Cu, Au), networks of noble metal (Au, Ag) nanoparticles or layers of robust bacterial biofilms have been considered.

We are also going to demonstrate that the photoinduced electron from semiconductor conduction band is capable of activation of the active center of the metalo-enzyme molecule. Here the.nanostructured silicon material has been chosen as the substrate for the enzyme adsorption. In this case the p-type Si(111) was etched toward formation of the bunched steps on the surface. The photo-biocathode with Cu-containing enzyme has induced the reduction of not only oxygen but carbon dioxide as well, under illuminations with photon energies higher than silicon band gap.

In the presentation, special attention will be paid to mechanistic aspects of electroreduction of carbon dioxide, fabrication and characterization of highly selective and durable semiconductor photoelectrode materials and to importance of the reaction conditions.

Study of electrochemical CO_2 reduction over WO_3 electrodes in aprotic media

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The current atmospheric levels of carbon dioxide and the diminution of fossil fuel reserves raise serious concerns about the resulting effects on the global climate change and on the future energy sources.

The CO_2 molecule is stable with a closed-shell electronic configuration and linear geometry[1]. Transitions metals and some of their compounds, such as metal oxides, are the most used substrates in (photo)electrocatalysis for CO_2 reduction. In fact, these materials have reactive electrons and vacant d orbitals, being able to provoke the activation of the CO_2 molecule by inducing the formation of the $CO_2^{\delta\cdot-}$ adduct and by facilitating the desorption of the reduction products[2].

WO_3 is an interesting material exhibiting a large variety of useful properties for different technological applications. It is probably the most studied electrochromic material and it can be reduced either chemically or electrochemically to form intensely colored compounds. However, these properties depend strongly on morphology of the material.

The aim of this communication is to present a study on the carbon dioxide electroreduction over nanostructured WO_3 electrodes in both humid and dry acetonitrile media, using electrochemical and spectroelectrochemical measurements (Fig 1). This provides an effective way to obtain direct information about the CO_2 reduction reaction and a concomitant electrochromic effect for WO_3 electrodes. Water content in the media is an important aspect in the CO_2 reduction, and thus in some experiments an extensive process for drying the acetonitrile has been used. Analysis of products of CO_2 reduction by gas chromatography shows CO as being the main product.

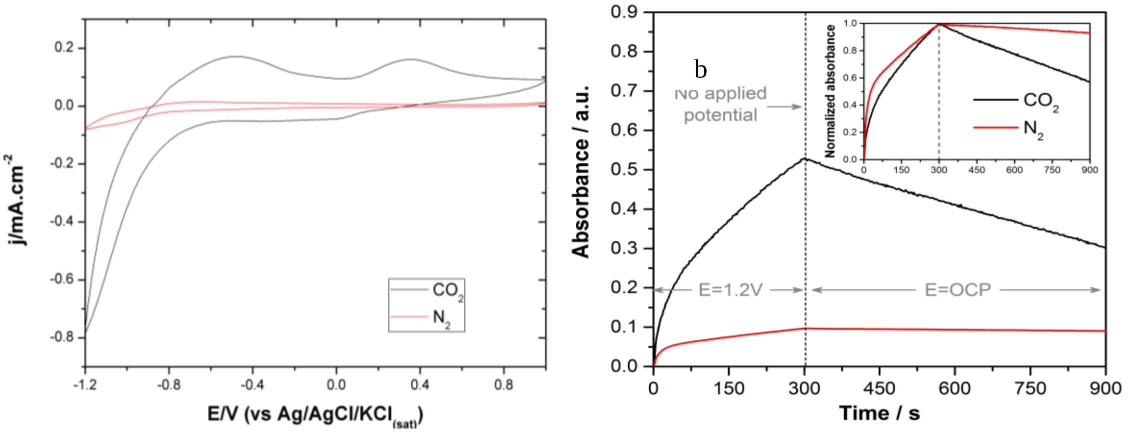

Figure 1. (a) Cyclic voltammograms for conducting glass (FTO)/WO_3 electrodes in 0.1M TBAP in acetonitrile. Scan rate: 50 mV s^{-1}. **(b)** Absorbance at 700nm as a function of time for a conducting glass (FTO)/WO_3 electrode in 0.1M TBAP/acetonitrile solution. Black and red curves correspond to the electrolyte purged with CO_2 and N_2, respectively.

References

[1] H.-J. Freund and M. W. Roberts, *Surf. Sci. Rep.*, vol. 25, no. 8, pp. 225–273, 1996.
[2] V. P. Indrakanti, J. D. Kubicki, and H. H. Schobert, *Energy Environ. Sci.*, vol. 2, no. 7, pp. 745–758, 2009.

Innovative photoelectrochemical cells based on polymeric membrane electrolytes and suitable porous photoanodes

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Photoelectrochemical (PEC) splitting of water by the direct use of sunlight is an ideal, renewable method of hydrogen production [1]. The majority of PEC cell studies utilize aqueous solutions as both the electrolyte and the photoanode reactants. Only few studies have attempted to separate the two half reactions compartments with a polymeric electrolyte membrane (PEM). In most of these cases acidic and alkaline solutions are used as anode reactants [2,3], but little work has been done with gaseous feedstock for the anode [4]. In our study we used solid-state electrolytes in conjunction with gaseous reactants in a PEM-PEC cell. Such system shows potential advantages over the liquid ones such as operation at higher temperatures and pressures (for improving the electrode kinetics), direct production of compressed H_2, compact and robust design besides the separation of the products at the electrode compartments. Moreover, it allows a water “neutral” operation, in which water is captured from the humidity in the ambient air.

Typically in PEM-PEC studies the powder photocatalyst is dispersed on the porosity of carbon supports (to ensure electronic conductivity) [4]. This choice presents two main disadvantages: (i) the formation of many photogenerated species recombination pathways at the powder grain boundaries and (ii) poor stability after prolonged operation, since the photocatalytic powder may become unbound to the substrate. To overcome these issues, we have successfully demonstrated an alternative design for PEM-PEC photoelectrodes, which utilizes a Ti-web of microfibers as starting material. Electrochemical anodization of this substrate has led to the fabrication of TiO_2 nanotubes arrays. In order to enhance the scope of application of our system to the visible domain of sun light, we chose to modify our TiO_2 electrodes with lower band-gap semiconductors. It has been shown in the literature that the addition of a WO_3 layer on TiO_2 leads to an increase of the current along with a redshifted light absorption. Furthermore it is also well known that $WO_3/BiVO_4$ association leads to some of the most visible light active photoanodes [5].

We have developed photoanodes which are based on the double junction $TiO_2/WO_3/BiVO_4$. Since the porous nature of the titanium substrate prevents the use of conventional techniques such as spin coating, an alternative fabrication method was developed. The protocol involves sputtering of W, followed by anodization and then by successive ionic layer adsorption and reaction (SILAR) method for $BiVO_4$ deposition [6]. In this way we were able to create the desired double junction and the synergies between the different layers were studied by photoelectrochemistry.

The performances of the TiO_2/WO_3 and $TiO_2/BiVO_4$ assemblies at acidic environment remained quite limited with a maximum photocurrent of ~0.1 mA/cm^2. But the full association $TiO_2/WO_3/BiVO_4$ gave a significant magnification of the current to reach ~0.4 mA/cm^2 (Figure 1). Work is in progress for enhancing the current densities by tuning the amount and the uniformity of $BiVO_4$ on the TiO_2/WO_3. Protecting layers are planned for utilizing membranes with alkaline environment polymeric membranes, since evaluation at mild alkaline conditions in liquid solutions results in very enhanced performance.

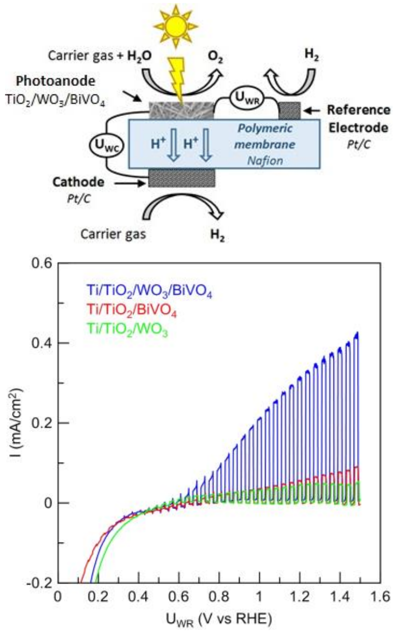

Figure 1: Linear sweep voltammograms of the WO_3, $BiVO_4$ and $WO_3/BiVO_4$ on Ti/TiO_2 porous substrates under simulated AM1.5 solar light at the chopped (On/Off) light condition at pH=1.

References

[1] A. Fujishima, K. Honda, Nature, 238 (1972) 37.
[2] B. Seger et al, J.Mater. Chem., 22 (2012) 10709.
[3] Y. Li et al, Int.J. Hydr. Energy, 36 (2011) 14374.
[4] T. Stoll et al, Int.J. Hydr. Energy, 41 (2016) 17807.
[5] P.M. Rao et al, Nano Lett.,14(2) (2014) 1099.
[6] Q. Jia et al, PNAs, 109, 29 (2012) 11564.

Photoelectrochemical CO_2 reduction at nanostructured gold/copper structures on Silicon

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Due to its unique properties copper is the most promising electrode material for the electrochemical reduction of CO_2 to CO, ethylene and methane; the product distribution sensitively depends on the electrode surface and the reaction conditions [1].

In order to achieve the direct conversion of solar into chemical energy we want to integrate copper nanostructures into a silicon photoelectrode. We approach such a system by structuring a silicon substrate with chessboard arrays of gold nanodisks which are electrochemically plated by copper.

In our work we examine how doping, illumination, structure size and copper coverage influence the potential distribution and mass transport. This is done by interpretation of changes in the electrochemical behavior and the product distribution measured by gas chromatography.

Additionally, we show that our structures feature surface plasmon polaritions (SPPs) which can be tuned from the visible into the mid-IR range using a bi-layer nanoimprint lithography method [2]. These SPPs enhance the electric field close to the metal surface [3], which is predicted to strengthen the adsorption of reactants and to polarizing adsorbates leading to lower overpotentials and a higher selectivity.

[1] Y. Hori, K. Kikuchi and S. Suzuki, Chem. Lett., 1695-1698 (1985).
[2] R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer and P. Lugli, submitted.
[3] S. Sun, W. Wang, L. Zhang, M. Shang and L. Wang, Cat. Comm. 11, 4, 290-293 (2009).

Atomic Layer Deposition of MoS_2 on Self-Supported Cu Substrate as Efficient Catalysts for Hydrogen Evolution

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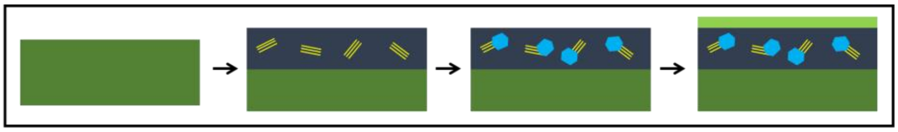
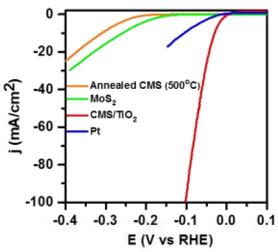
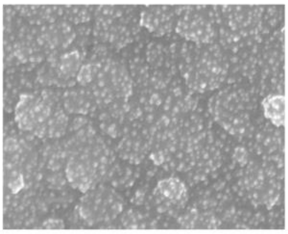
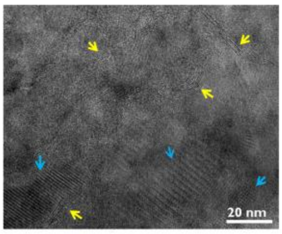
The edge sites of MoS_2 have been shown to be efficient electrocatalysts for the hydrogen evolution reaction (HER) replacing expensive noble metals, e.g., Pt. Here, we first describe that when atomic layer deposition (ALD) is applied to layered materials such as MoS_2. MoS_2 exhibits the non-ideal mode of ALD growth on planar surfaces. As a model system, the ALD of $MoCl_5$ and H_2S was studied. This non-ideality does not allow for the conventional linear relationship between the growth thickness and the number of cycles. Instead, it provides the ability to control the relative ratios of the edge-sites and basal planes of MoS_2 to the exposed surfaces. The number of edge sites produced was carefully characterized in terms of the geometric surface area and effective work function and was correlated to the HER performance, including Tafel slopes and exchange current densities. When MoS_2 as a representative 2-D material is deposited on transition metals such as Cu in a controlled manner, the sulfidation reactions also occur with the metal. We observed the spontaneous formation of a composite chalcogenide materials that consist of two-dimensional (2-D) materials dispersed in bulk, i.e., bulk layered heterojunctions (BLHJs) of Cu-Mo-S that contain MoS_2 flakes inside, which are uniformly dispersed in the Cu_2S matrix, and their unusual charge transport properties for application in hydrogen evolution reactions (HERs). The resulting structures were expected to induce asymmetric charge transfer via layered frameworks and tested as electrocatalysts for HERs. Upon suitable thermal treatments, the BLHJ surfaces exhibited the efficient HER performance of approximately 10 mA/cm^2 at a potential of as low as -0.1 V versus a reversible hydrogen electrode (RHE). The Tafel slope was approximately 30 to 40 mV/dec. The present strategy was further generalized by demonstrating the formation of BLHJs on other transition metals such as Ni. The resulting BLHJs of Ni-Mo-S also showed the remarkable HER performance and the stable operation over 10 days without using Pt counter electrodes by eliminating any possible issues on the Pt contamination.









Electrochemistry of High Ion Flux Helium Plasma-exposed Iron Oxide Thin Films

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Hematite (α-Fe_2O_3) is an attractive material for the oxygen evolution reaction (OER), especially due to its chemical stability, non-toxicity, abundance and low cost [1]. Although it has various advantages, the low water splitting efficiency of hematite films has hampered its use in commercial water splitting efforts. The low efficiency is an outcome of two major limitations. The first is the poor absorptivity of hematite as a result of the indirect nature of its bandgap and the second is the short minority carrier diffusion length (2-4 nm) in hematite films [2]. The former requires relatively thick films (400-500 nm) while the latter requires much thinner films in the range of 20-50 nm. This apparent incongruity can be solved by nanostructuring in order to create thin films with a large surface area. This then allows us to maximize the light absorption while insuring a high charge collection efficiency. One way to obtain controlled nanostructuring of iron oxide thin films is by high ion flux helium plasma exposure [3].

In the following work, we study the physical, chemical and photo-electrochemical (PEC) properties of the plasma-exposed iron oxide films [4]. Thin films with high degree of nanostructuring are obtained on plasma exposure, as can be seen in figure 1(a). Plasma exposed films are also seen to contain multiple iron oxide phases, including α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4. Electrochemical impedance spectroscopy (EIS) is used to relate the PEC water splitting activity of the plasma-exposed films to their morphology and chemical composition. Fitting of the EIS data to an equivalent circuit model allows us to demonstrate that the increase in PEC activity of the plasma-exposed films can be attributed to two factors. Firstly, an increase of up to 40 times in the active surface area on plasma exposure as compared to unexposed films, as represented by the bulk capacitance values in figure 1(b). Secondly, the presence of γ-Fe_2O_3, which provides a second OER pathway for water splitting at high potentials. This is made possible due to a rapid drop in the charge transfer resistance for OER through the γ-Fe_2O_3 with increase in applied potential, as seen in figure 1(c). Combination of these two factors leads to 5 times increase in the photocurrent density for plasma-exposed films over unexposed films.

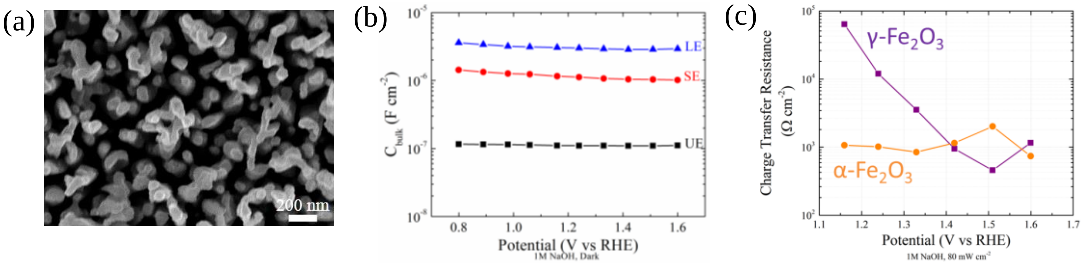

Figure 1(a) Top-view SEM micrograph of iron oxide thin film LE after high ion flux helium plasma exposure for 50 min and annealing at 645 °C in air for 10 mins; (b) Bulk capacitance values obtained from fit of impedance data for thin films: unexposed film UE(■), short exposed film SE (•) and long exposed film LE (▲); (c) Charge transfer resistance for OER in plasma-exposed film SE via α-Fe_2O_3 surface (•) and γ-Fe_2O_3 surface (■). All measurements were performed in 1M NaOH.

[1] Sivula K., Le Formal F., Grätzel M., ChemSusChem (2011) 4 432
[2] Zandi O., Hamann T. W., Phys Chem Chem Phys (2015) 17 22485
[3] Bieberle-Hütter A., Tanyeli I., Lavrijsen R., Koopmans B., van de Sanden, M. C. M., Thin Solid Films (2016) Submitted
[4] Sinha R., Tanyeli I., Lavrijsen R., Koopmans B., van de Sanden M. C. M., Bieberle-Hütter A., J. Phys. D: Appl. Phys. (2016) Submitted

Experimental and theoretical investigation of Prussian blue type redox catalysts for artificial photosynthesis

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The development of an efficient, cheap and robust water-oxidaton catalyst remains the bottleneck step to realizing artificial photosynthesis. Materials based on Prussian blue (iron hexacyanoferrate), which fulfill all those criteria, have shown high catalytic activities with exceeding long-term stabilities.[1],[2] In combining experimental methods with theoretical calculations we aim to elucidate the underlying photo-physical mechanisms and its determining factors.

Catalytic systems were prepared by modifying the well-known photo-catalytic material $BiVO_4$, with cobalt iron analogues of Prussian blue (CoFe-PB), which largely increases the photocurrent and significantly lowers the onset potential of light-induced water oxidation. (see Figure 1a) Different experimental data, such as impedance spectroscopic data, indicate that the CoFe-PB catalytic system acts as a true hole-transfer catalyst. This is supported by preliminary theoretical calculations based on hybrid density functional theory.

It was found that common density functional theory (DFT) methods are insufficient to accurately describe the complex electronic and magnetic structure of Prussian blues and functionals of higher degree of complexity are needed. We developed a robust computational scheme to evaluate electronic structure relationships of the combined semiconductor system, which might be crucial to its photo-catalytic applications. [3]

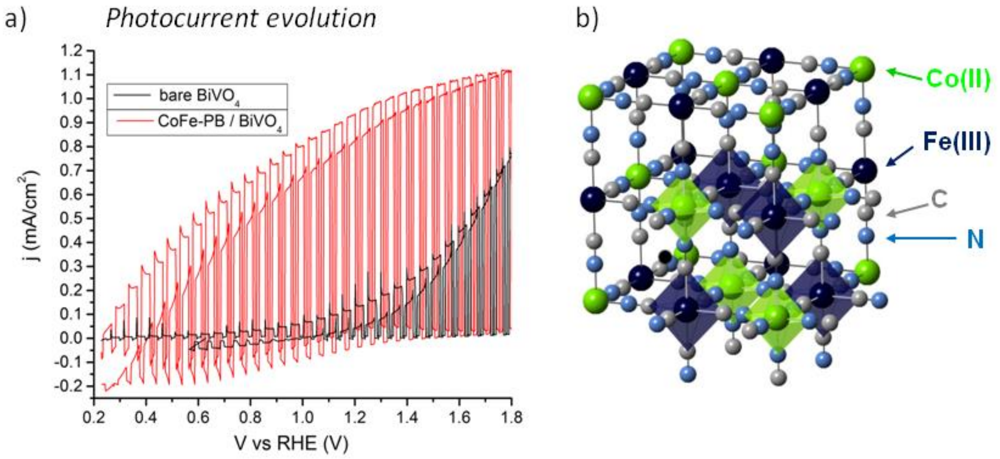

Figure 1: *a) Cyclic voltammogram (scan rate 50 mV/sec) of a bare and modified $BiVO_4$ photoanode under chopped light (1 sun) at pH 7 (0.1 M KPi buffer). b) Idealized fcc crystal structure of the CoFe-PB catalyst*

References:

[1] Goberna-Ferrón, S.; Hernández, W. Y.; Rodríguez-García, B.; Galán-Mascarós, J. R. Light-Driven Water Oxidation with Metal Hexacyanometallate Heterogeneous Catalysts. *ACS Catal.* **2014**, 4, 1637.

[2] Pintado, S.; Goberna-Ferrón, S.; Escudero-Adán, E. C.; Galán-Mascarós, J. R. Fast and Persistent Electrocatalytic Water Oxidation by Co-Fe Prussian Blue Coordination Polymers. *J. Am. Chem. Soc*. **2013**, 135, 13270.

[3] Hegner, F. S.; Galán-Mascarós, J. R.; López, N. A Database of the Structural and Electronic Properties of Prussian Blue, Prussian White, and Berlin Green Compounds through Density Functional Theory, *Inorg. Chem.* **2016**, in press: DOI: 10.1021/acs.inorgchem.6b02200

Silver nanoparticles/nanostructured TiO_2 interface: a photo-renewable “silver-ions electrode” for neurotransmitters detection

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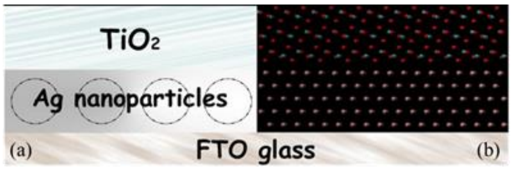
Silver nanoparticles were embedded in a TiO_2 (anatase polymorph) photoactive layer in a sandwich-like nanostructured electrode. [1-2]



The device was (photo)electrochemically characterized by cyclic voltammetry and electrochemical impedance spectroscopy.

In comparison with literature data on electrodes modified with silver nanoparticles [3-5], the new sensor presents a pronounced electrocatalytic effect on the silver oxidation peak together with a great increase in the current intensity.

Parallel plane-wave DFT calculations, performed using the VASP code [6], described the composite junction as a distorted bulk Ag structure, commensurate with the periodicity of the (101) face of the $I4_1/amd$ TiO_2 anatase polymorph. The silver atoms close to the semiconductor were found to gain a partially positive charge, quickly decreasing with the distance from the TiO_2 surface.

Comparing the theoretical and experimental results it could be concluded that the device may be considered as a “positively charged silver nanoparticles-based electrode”, with positively ionized surface silver atoms protected by the titania layer, which holds a partial negative charge.

The final sensor performed efficiently in the electroanalytical determination of some neurotransmitters (e.g. dopamine, norepinephrine and serotonin) in simulated biological matrices (liquor, serum and urine). The optimized analytical methodology is not only characterized by high sensitivity and low detection limits (around 0.03 µM, which makes it appealing for clinical purposes), but also by high selectivity in the presence of high concentrations of conventional interferents (uric and ascorbic acids).

Last but not least, the fouling and passivation of the electrode surface, an unavoidable drawback during the detection of this kind of analytes, could be easily overcome by irradiating the device with UVA-light, which restored the initial sensor sensitivity. The photo-renewability allows to reactivate the sensor on site, *i.e.* directly in solution, to yield a system capable of working in continuous, able to be used in an integrated monitoring system.

References

[1] G. Soliveri, V. Pifferi, G. Panzarasa, S. Ardizzone, G. Cappelletti, D. Meroni, K. Sparnacci, L. Falciola, Analyst, 140, (2015), 1486 – 1494.
[2] V. Pifferi, G. Soliveri, G. Panzarasa, S. Ardizzone, G. Cappelletti, D. Meroni, L. Falciola, RSC Advances, 5, (2015), 71210 – 71214.
[3] O. S. Ivanova, F. P. Zamborini, J. Am. Chem. Soc., 132, (2010), 70–72.
[4] G. Chang, J. Zhang, M. Oyama, K. Hirao, J. Phys. Chem. B, 109, (2005), 1204-1209.
[5] S.E. Ward Jones, F.W. Campbell, R. Baron, L. Xiao, R.G. Compton, J. Phys. Chem. C, 112, (2008), 17820–17827.
[6] G. Kresse, J. Furthmüller, Phys. Rev. B, 54:11169, (1996).

Acknowledgements

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A high contrast complementary electrochromic device based on two conducting polymer thin films

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A complementary electrochromic device (ECD, with an active area of 1.0 cm x 1.0 cm), composed of an anodically coloring poly(N′,N″,N‴-tris[N,N-bis-(4′-diphenylamino-biphenyl-4-yl)phenyl]-1,3,5-benzene-tricarboxamide) (PG1) thin film with 5 mC electrodeposited charge and a cathodically coloring poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-Et_2) thin film with 40 mC electrodeposited charge, has been fabricated. The proposed ECD exhibits sub-second response time of less than 0.2 s and conspicuous transmittance change of 53.5% at 590 nm. The stability test of the ECD reveals negligible decay in the transmittance change and maintains 96.9% of its initial transmittance change after continuous 10,000 cycles at room temperature. In order to understand the mechanism behinds its electrochromic switching and stability, an electrochemical quartz crystal microbalance (EQCM) is coupled with cyclic voltammetry (CV) to better understand the ionic transport processes occur within both thin films.

Table 1 Electrochromic properties of the two conducting polymer thin films.

electrochromic material	λ_{max} (nm)	V_b/V_c (V)	τ_b/τ_c (s)	T_b/T_c (%)	ΔT (%)
PG1	850	0/0.8	1.8/2.3	80.0/42.9	37.1
PProDOT-Et_2	590	0/-0.8	0.64/0.87	76.1/14.8	61.3

Table 2 Performance of the ECD.

ECD	λ_{max} (nm)	V_b/V_c (V)	τ_b/τ_c (s)	T_b/T_c (%)	ΔT (%)	Cycling stability (%)
PG1/PProDOT-Et_2	590	-0.2/1.2	0.13/0.18	62.1/8.6	53.5	96.9

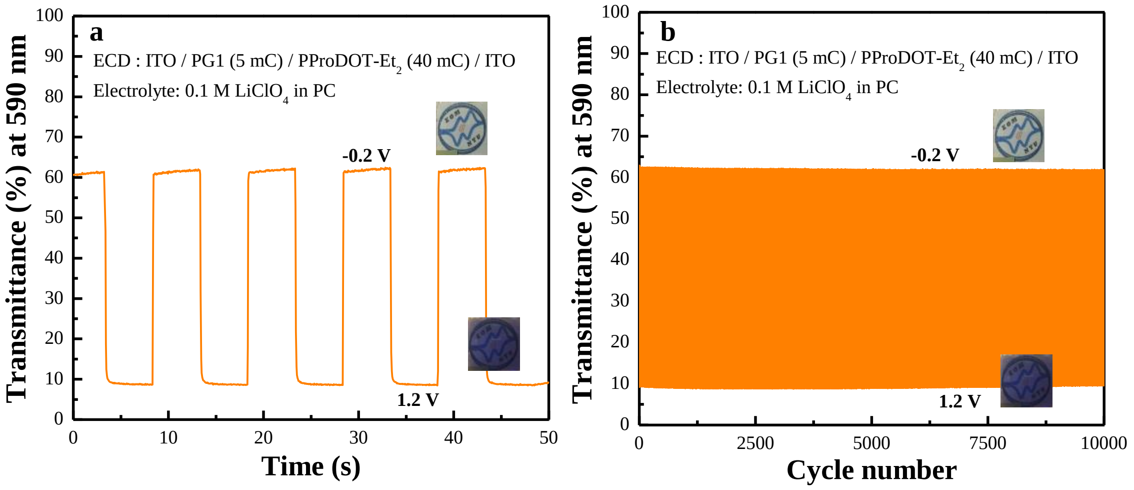

Fig. 1 (a) Dynamic transmittance curves for the PG1/PProDOT-Et_2 ECD switched at +1.2 V and -0.2 V with an interval of 5 s. (b) Cycling stability data for the PG1/PProDOT-Et_2 ECD with a switching interval of 2 s.

Why Should Photocatalysts be Semiconductor? – Roles of Electron Traps in Metal Oxide Particles

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Heterogeneous photocatalysis in which a particulate photocatalyst is suspended in a solution or placed in contact with a substrate (substrates) in a gas phase and irradiated has been one of the important topics in chemical, energy-related and environmental sciences. This heterogeneous photocatalysis has often been called "semiconductor photocatalysis". This might be because most of known/used photocatalysts, e.g., titanium(IV) oxide (titania) and cadmium sulfide, are categorized into semiconductors among materials. In the history of photocatalysis studies, the discovery of photoassisted electrochemical splitting of water with a single-crystal titania electrode and a platinum counter electrode under electrochemical/chemical bias potential application [1] has accelerated research on heterogeneous photocatalysis using particulate metal oxides. In electrochemical cells, semiconductor single-crystal electrodes that were reduced to give conductivity by introducing donor levels between conduction band (CB) and valence band had been used. When these electrodes of n-type semiconductors are in contact with electrolyte solutions, electrons in the donor levels flow out, due to their relatively high Fermi level, to the solution to give "a depletion layer" of an electric field, where a photoexcited electron in the CB and a positive hole in the VB migrate in opposite directions: electrons to the surface and holes to the bulk. This Schottky-type barrier is one of the significant features of a semiconductor-electrolyte solution interface and it was believed, at least in the 1980's, that the depletion layer is the reason for the high efficiency of "semiconductor photocatalysis". In this sense, it seemed reasonable to call heterogeneous photocatalysis "semiconductor photocatalysis". However, it was pointed out in the 1990's that the density of impurities for donor levels in ordinary particulate photocatalysts is too low to establish an electric field gradient within the particles, i.e., the expected depth of the depletion layer is larger than the actual particle size. Thus, Schottky type-barrier formation in the photocatalyst-solution interface has not been assumed, and a simple mechanism in which reduction and oxidation by photoexcited electrons and positive holes, respectively, proceed with surface-adsorbed substrates has been used for the interpretation of heterogeneous photocatalysis in almost all of the recent publications in this field. It should be noted that characteristics of (n-type) semiconductors disappeared in this simple model, i.e., the photocatalyst materials can be insulators having an electronic structure composed of a filled VB and vacant CB as of semiconductors. Then, how can we explain the very low or negligible photocatalytic activities of insulators such as aluminum oxide (alumina) and silicon oxide (silica)? [2]

As has been proposed an the author's review [3], it can be assumed that semiconducting properties, especially n-type ones, to give electron traps (ETs) are essential for particulate photocatalysts. Although the density in the particulate photocatalysts described above might be very low, impurities (or surface structure) to give donor levels may exist at least at a detectable level, and electrons in those levels may flow out, like those in semiconductor electrodes, to an electrolyte solution that is in contact with photocatalyst particles to result in the formation of electron-deficient vacant levels, *i.e.*, ETs to accept electrons. If the depth, i.e., the difference in energy between the CB bottom (CBB) and ETs, is smaller than the thermal energy of electrons (0.026 eV = 26 meV at 300 K), electrons in these shallow traps can be thermally excited to the CB and be trapped again in another ET, i.e., electrons can migrate through the CB and shallow ETs at a speed that might be faster than electron hopping between ETs. On the other hand, if ETs are located deeply, electrons once trapped by these deep ETs cannot be excited thermally to the CB and just recombine with a positive hole. Thus, as a working hypothesis, it can be assumed that shallow and deep ETs enhance and reduce photocatalytic activity of particles by migration of electrons through CB–ETs and electron–positive hole recombination, respectively. In this sense, photocatalysts should be of semiconductors but not insulators possessing no ETs, and the energy-resolved distribution of ETs (ERDT) in particulate photocatalysts may be one of the decisive factors governing their photocatalytic activities. A recent results on ERDT in metal-oxide photocatalysts [4] are discussed in this presentation.

[1] Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38. [2] Ohtani, B. *Catalysts* **2013**, *3*, 942–953. [3] Ohtani, B. *Catalysts* **2016**, *6*, 192-197. [4] Nitta, A.; Takase, M.; Takashima, M.; Murakami, N.; Ohtani, B. *Chem. Commun.* **2016**, *52*, 12096–12099.

The role of supporting electrolyte in the kinetic of photocatalytic processes: using the electrochemical approach for probing its effect on reactions at the interface of nanoparticulate P25 TiO_2

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It is a matter of fact that electrodes comprising nanoparticles of an intrinsic semiconductor do not present band bending [1]. Thus, the semiconductor never leaves the flat band condition, and the application of a biasing potential merely accomplishes the collection of long living carriers, which usually are the electrons for TiO_2 [2]. In such a case, the rate of capture of photoholes (h^+) at the interface controls the film conductivity under a constant irradiant flux, and the photocurrent (iph) measured under high enough biasing potential is related to the kinetics of different oxidation sites on the particles. Apparently, the supporting electrolyte presents influence on this dynamic of photoholes (**Fig. 1**).

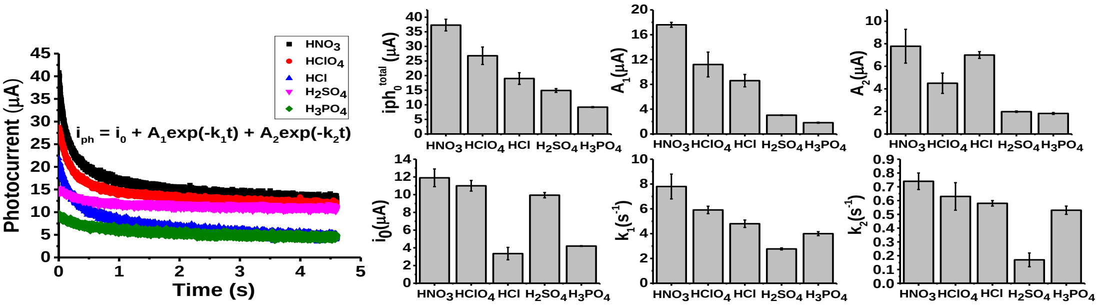

Fig. 1 – Chronoamperograms recorded at +0.5 V *vs.* Ag/AgCl(3.5 mol L^{-1} KCl) under ~91 mW cm^{-2} of UV (365 nm) radiant flux for a variety of 0.1 mol L^{-1} acids in pure water. The equation was fitted ($R^2 > 0.9$) using the program Origin® 2016. The histograms comprise the values of variables for triplicates.

The double exponential decay function (**Fig. 1**) presents a reasonable fit to describe the behavior of photocurrent recorded during the execution of chronoamperograms at constant applied potential (+0.5 V *vs.* Ag/AgCl) and UV randiant flux (~ 91 mW cm^{-2}). The i_0 parameter describes a constant process occurring at the electrode during the whole experiment and is related with the H_2O oxidation. The existence of two exponential components suggests two types of complexing surface sites with different reaction rates, the first one corresponding to a faster process, with higher exponential constants (k_1). All the electrolytes were tested in acidic medium (0.1 mol L^{-1}; pH < 2). Using the initial photocurrent (iph→0 s) as a first parameter, a decreasing tendency is observed: $HNO_3 > HClO_4 > HCl > H_2SO_4 > H_3PO_4$. This difference might be explained in terms of the competitive adsorption of the respective anions with water and the formation of different hole traps. HNO_3 and $HClO_4$ are known to present unspecific interaction with the TiO_2 surface, with major contribution of the reactive sites (60-68 %) on the total initial iph. HCl presents a weak interaction with TiO_2 too, with greater predominance of the sites contributing to the total initial iph of oxidation (82 %). This unbalanced relationship of the photocurrent is caused by the low organization of water on the surface in the presence of hydrated Cl^- [3], leading to a low contribution of water oxidation to the total iph amount. H_3PO_4 and H_2SO_4, in turn, are known to possess a much stronger interaction with TiO_2 surface [4]. Their initial total iph values are much lower than for the other anions. For H_3PO_4, the contribution of both water and sites is similar, while for H_2SO_4 almost 70 % of the total initial iph comes from the water oxidation. Finally, the analysis of exponential constants reveals that the kinetic of the sites reactivity is strongly hindered by the SO_4^{2-} (and HSO_4^-) anion(s) and significantly decreased for phosphoric acid anions, pointing out to a possible formation of deeper hole traps that compromise the photohole dynamics.

References

[1] A. Hagfeldtt, M. Grätzel, Chemical Reviews 95 (1995) 49.
[2] A. Fujishima, X. Zhang, D.A. Tryk, Surface Science Reports 63 (2008) 515.
[3] S. Kataoka, M.C. Gurau, F. Albertorio, M.A. Holden, S-M. Lim, R.D. Yang, P.S. Cremer, Langmuir 20 (2004) 1662.
[4] V.E. Kazarinov, V.N. Andreev, A.P. Mayorov, Journal of Electroanalytical Chemistry 130 (1981) 277.

Influence of Cd/Mn ratio on the photoelectrochemical properties of $Cd_{1-x}Mn_xS/Bi_2S_3$ co-sensitized boron-doped TiO_2 nanotubes

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The energy conversion efficiency in a solar cell mainly depends on the improved light harvesting of photons in a wide solar spectrum range and the photocurrent generation which is associated to the facility of photogenerated electrons flow into the device [1]. However, it is important understand how the band edge alignment between a wide-band gap semiconductor as TiO_2 and metal chalcogenides used as sensitizers in quantum dot sensitized solar cells can benefit or detriment the electron mobility through the photoanode before to assembly a photovoltaic device [2]. In this contribution, we studied the effect of depositing a ternary chalcogenide based on cadmium and manganese sulfide ($Cd_{1-x}Mn_xS$), on the photoelectrochemical performance of boron-doped TiO_2 nanotubes/$Cd_{1-x}Mn_xS/Bi_2S_3$ heterostructure under visible light, varying the Cd/Mn ratio in the ternary compound. The morphology, optical properties and chemical environment of composed photoanodes were investigated by FESEM, TEM, DRS and XPS, while their photoelectrochemical and semiconducting properties were characterized by photovoltammetry, photocurrent transient measurements and Mott-Schottky analysis. Boron-doped TiO_2 nanotubes (B-TNT) sensitized with CdS QDs shows an increase of photocurrent than that pristine TNT and unsensitized B-TNT as a clear increment of photogenerated electron injection from CdS, displacing the open circuit potential (OCP) to more negative values. Nevertheless, after Bi_2S_3 QDs sensitization, both OCP and photocurrent were decreased. This could correspond to an unsuitable band alignment between CdS and Bi_2S_3, hindering the electron flow in the CdS/Bi_2S_3 interface and thereby decreasing the photoresponse of material. To exchange Cd^{2+} by Mn^{2+} cations to obtain a Cd/Mn ratio: 1.0 in the $Cd_{1-x}Mn_xS$ sensitizer, the OCP and photocurrent of material is increased again (Fig.1a) due to the formation of Mn^{2+} energy levels into chalcogenide [3], matching with the CB of Bi_2S_3 in an adequate II-type band alignment (Fig.1b). The ternary compounds can be used to tune metal chalcogenides what present a high low-energy light harvesting but not exhibit a suitable band alignment with other sensitizers or TiO_2, affecting negatively the photovoltaic efficiency.

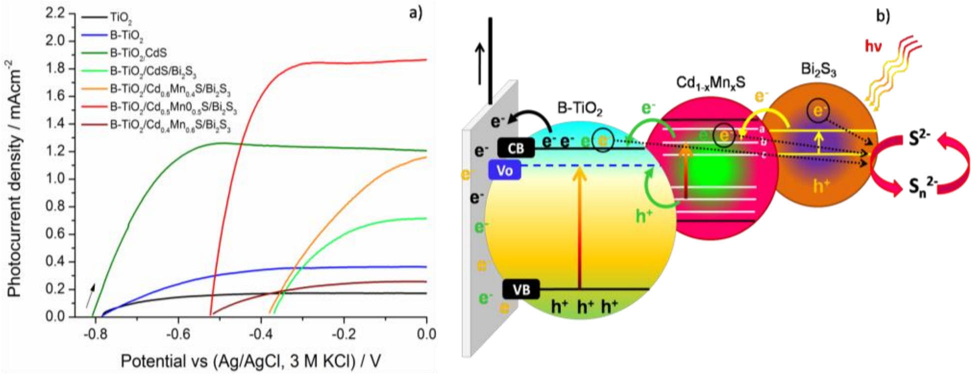

Fig.1. Photovoltammograms performed at 10 mV s^{-1} in 0.25 M Na_2S and 0.35 M Na_2SO_3 a) and Schematic representation of interfacial charge carrier transport and recombination in B-TNT/ $Cd_{1-x}Mn_xS/Bi_2S_3$ based photoanodes b); a, b, and c indicates the Cd/Mn ratio of 0.7, 1.0 and 1.5, respectively.

[1] S. A. Pawar, D. S. Patil, H. R. Jung, J. Y. Park, S. S. Malic, C. K. Hong, J. C. Shin, P. S. Patil, J. H. Kim, Electrochim. Acta, 203 (2016) 74.
[2] L. Yu, Z. Li, Y. Liu, F. Cheng, S. Sun, Appl. Surf. Sci., 309 (2014) 255.
[3] P. K. Santra, P. V. Kamat, J. Am. Chem. Soc., 134 (2012) 2508.

Microstructuration of Silicon Surfaces Using Nanoporous Gold Electrodes

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Etching is a key process in the fabrication of silicon (Si) microstructures that are essential for several component families used in microelectronics, photonics and photovoltaics, among others. A large variety of microstructuring technologies exists nowadays (e.g. wet/dry etchings based on photo/electron beam lithography patterning). Their remarkable efficacy comes at the expense of several lithography (masking) /etching steps that are not suitable for all industries, i.e. when reduced cost and manufacturing time are key aspects (e.g. Si solar cells manufacturing). Hence, the development of a maskless technique with direct imprinting of patterns would dramatically simplify the fabrication process. However, eliminating the use of masks and move towards micromachining techniques has turned to be extremely challenging. Only a few achievements in the field of (electro)chemistry have been reported in the literature [1-4].

The most recent development is an electrochemical version of the *metal assisted chemical etching* method used to produce high aspect ratio nanostructures: a noble metal electrode is put in contact with a Si sample in a HF solution and polarized against a counter electrode; in the contacted areas the metal plays the role of etching tool by oxidizing/dissolving Si atoms [2,3]. The major problem encountered with this configuration lies in the intimate Si/metal contact, which hinders electrolyte supply over macroscopic distances. Hence, etching is very slow, starting from the edge of the metal tool and progressing laterally. An efficient pattern transfer has been recently demonstrated in the case of porous Si etching with a gold coated stamp, the porous Si network allowing the electrolyte to reach the Si/Au interface [4].

In this work, we present a new strategy to achieve pattern transfer into Si by a single step electrochemical (EC) contact etching with large dimension metal tools, as schemed in Figure 1a.

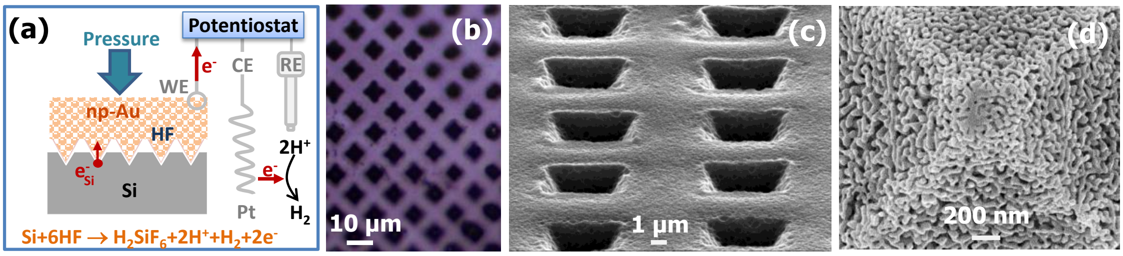

Figure 1. a) Scheme of the electrochemical contact etching process; b, c) optical and SEM images of a n-type (100) Si surface after imprinting a pattern of inverted pyramids with d) a nanoporous Au electrode.

The problematic diffusion of the electrolyte is solved by using for the first time nanoporous metal electrodes, which give access for the electrolyte to the whole Si/metal interface. Thus, etching is achieved with a priori no restriction on the dimensions of the treated surfaces.

Our first results demonstrate the transfer of a well-defined array of square inverted pyramids over a treated area of approximately 1 mm^2 (Figure 1b and 1c) in a single step and without any prior lithography or masking process of the substrate. The etched pyramids are not aligned with the [001] and [010] directions of the (100) oriented sample (21° off) which clearly indicate that the pattern transfer is independent of the crystallographic orientation. This is a proof of concept for EC contact etching with nanoporous metal imprints, with a high potential for Si surface texturization (e.g. solar cells) [5].

[1] P. Allongue, P. Jiang, V. Kirchner, A.L. Trimmer, R. Schuster *J. Phys. Chem. B*. 108 (2004) 98.
[2] T. Sugita, C.-L. Lee, S. Ikeda, M. Matsumura *ACS Appl. Mater. Interfaces* 3 (2011) 2417.
[3] T. Fukushima, A. Ohnaka, M. Takahashi, H. Kobayashi *Electrochem. Solid-State Lett*. 14 (2011) B13.
[4] P. Azeredo, Y. Lin, A. Avagyan, M. Sivaguru, K. Hsu, P. Ferreira *Adv. Func. Mater*. 26 (2016) 2929.
[5] E. Torralba et al. *ACS Appl. Mater. Interfaces* 8 (2016) 31375.

Hierarchical ZnO nanostructures engineering: influence of surface morphology on photocatalytic and photoelectrochemical Performance

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Recently, due to the climate change and the depletion of the fossil reserves, extensive investigations have been carried out to develop an alternative clean and abundant energy source. Solar energy is freely available clean energy and easily accessible among all renewable sources. Photocatalytic (PC) dye degradation process and photoelectrochemical (PEC) water splitting systems for H_2 production are sustainable approaches to overcome the energy and environmental challenges by using sunlight and a proper semiconductor. For the first time, the concept of PEC based on TiO_2 photocatalyst has been described by Fujishima and Honda in 1972 [1] and research in this field have grown extensively in the past decades.

In this research, a comparative study was conducted to elucidate the role of surface morphology on the photocatalytic and photoelectrochemical properties of hierarchical ZnO nanostructures. In this context, ZnO nanowires (NWs) were formed by using anodization of Zinc (99.98% purity) foil [2]. Hydrothermal method was used for engineering different ZnO hierarchical structures (HS-ZnO NWs). Different parameter involved in hydrothermal process was studied including reaction times 1 and 5h to compare their aspect ratios of the HS-ZnO NWs.

Different techniques, including field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRD), UV–visible diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) spectroscopy were employed to characterize the nanostructures. Figure 1 show FESEM images of the ZnO NWs, HS-ZnO NWs (1h) and HS-ZnO NWs (5h). Based on our DRS analysis, light scattering of the HS-ZnO NWs (5h) is more than the ZnO NWs and HS-ZnO NWs (1h) samples under similar visible irradiation. Photo degradation of methylene blue (MB) under UV light was evaluated and the HS-ZnO NWs showed an enhancement in photocatalytic activity as compared to the ZnO NWs due to its higher aspect ratio. PEC activity of the HS-ZnO NWs was also investigated under light illumination of 100 mW cm^{-2}. By using chronoamperometry technique, the photocurrent density for the HS-ZnO NWs (5h) photoanode was measured at about 90 $\mu A/cm^2$, without any applied bias voltage, which was 9 times higher than the ZnO thin film. Therefore, it was found that the HS-ZnO NWs with improved surface area and thus higher light absorption show effective redox reactions and will be promising system for the solar energy applications.

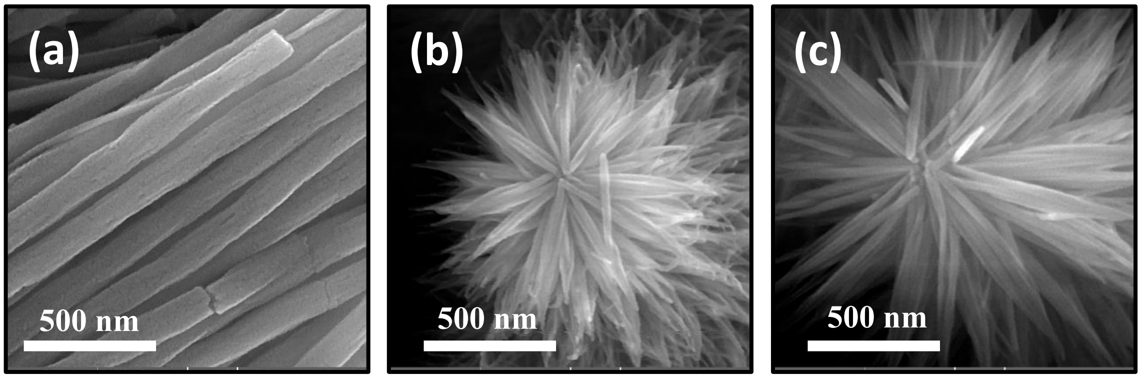

Figure1. (a) FESEM images of (a) ZnO NWs, (b) HS-ZnO NWs (1h) and (c) HS-ZnO NWs (5h).

[1] A. Fujishima and K. Honda, Nature **238**, 37 (1972).
[2] M. Ebrahimi, M. Samadi, S. Yousefzadeh, M. Soltani, A. Rahimi, T.-C. Chou, L.-C. Chen, K.-H. Chen, and A. Z. Moshfegh, ACS Sustainable Chem. Eng. (2016).

Plasmonic gold nanoparticles in Au/TiO_2 photocatalysts

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Incorporation of plasmonic metal (gold, silver) nanoparticles (NPs) into semiconductors is motivated by the will to change the optoelectronic properties of the photomaterials. Suspensions of titanium dioxide (TiO_2) particles are widely examined in the process of photocatalytic decomposition of organic pollutants in water and air [1]. Because of its band-gap energy of ca. 3.0 eV, the TiO_2 can be only excited by light of wavelengths shorter than 400 nm. Several different methods of enhancing absorption in visible range of light to improve photocatalytic efficiency of TiO_2 have been tested [2]. In this work, we have used thin film (rutile) TiO_2 photoelectrodes decorated with photodeposited or sputtered gold NPs. Modified electrodes were examined by scanning electron microscopy (SEM), UV-Vis spectroscopy and X-ray photoelectron spectroscopy (XPS). Due to the use of photoelectrodes we were able to conduct photoelectrochemical measurements in a system that simulates conditions of photocatalysis on powder suspensions. The presence of Au NPs on the TiO_2 surface clearly increased values of incident photon-to-current conversion efficiencies (IPCEs) in the processes of oxidation of organic species (e.g. acetic acid) over the range of wavelengths that are only negligibly absorbed by unmodified titanium dioxide (Fig. 1).

The obtained results revealed, however, a critical impact of the sample history on the photocatalyst activity, over repeated measurements, raising doubts on the long term stability of Au/TiO_2 photocatalysts employed to degrade organic contaminants in water.

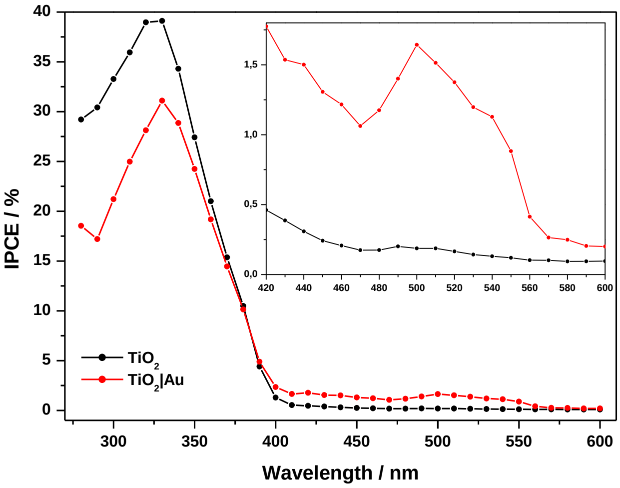

Figure 1. Incident photon-to-current efficiency-photoaction spectra, for TiO_2 (black) and Au/ TiO_2 (red), electrodes immersed in a 1 M aq. $NaClO_4$ with added 5 v.% CH_3COOH recorded at an imposed potential of: 0.4 V *vs* Ag|AgCl.

[1] J. M. Herrmann, *Top. Catal*. 2005, 34, 49-65.
[2] M. Pelaeza, N.T. Nolanb, S.C. Pillaib, M.K. Seeryc, P. Falarasd, A.G. Kontosd, P.S.M. Dunlope, J.W.J. Hamiltone, J.A. Byrnee, K. O'Sheaf, M.H. Entezarig, D.D. Dionysiou, *Appl. Catal., B: Environmental*, 2012, 125, 331-349.

Enhanced water splitting using tungsten trioxide–based photoanodes

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Semiconductor-tungsten trioxide (WO_3) films find application in a large variety of fields including photocatalysis, gas sensors, smart windows or as substrates for heterogeneous catalysts. Herein we will focus on recent improvements in optoelectronic and photoelectrochemical properties of WO_3 thin films achieved in our laboratory. Fabrication of nanostructured, mesoporous WO_3 films with thicknesses of the order of 1 micron or less provides particularly effective photoanodes for water and sea water splitting under visible (solar) light illumination. Such films are synthesized on fluorine-doped tin oxide (FTO) conductive glass substrates by a sol-gel method using as a precursor mixtures of tungstic acid with added dopants and organic structure-directing agents that allow achieving controlled porosity of the film. The porous structure of the films allows permeation of the electrolyte over the whole film thickness during water splitting experiments. Of equal importance is the annealing step of the as deposited samples, performed in oxygen above 500°C that ensures its structural ordering with formation of monoclinic WO_3 exhibiting excellent crystallinity. The latter is critical in reducing photogenerated charge recombination in the final photomaterials and obtaining large water photooxidation currents. Although the visible-light absorption range of the WO_3 films is still restricted to 500 nm, under standard conditions, including a bias of 1.23 V versus reversible hydrogen electrode (RHE) and simulated AM 1.5 solar light (100 mW/cm^2) illumination, stable oxygen evolution photocurrents exceeding 4 mA/cm^2 are regularly attained. This is due to the combination of the employed dopants in WO_3 and oxygen evolution reaction (OER) catalysts.

Acknowledgment

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[1] M. Sarnowska, K. Bieńkowski, P.J. Barczuk, R .Solarska, J. Augustyński, *Adv. Energy Mater.* **2016**, 1600526

[2] A. Jelińska, K. Bieńkowski, R .Solarska, M. Pisarek, J. Augustyński (submitted)

Light-Driven Electrocatalytic Reduction of CO_2 on Silicon Nanowires using Mn Bipyridyl Complex Catalysts

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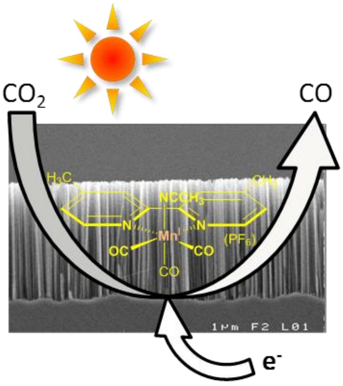
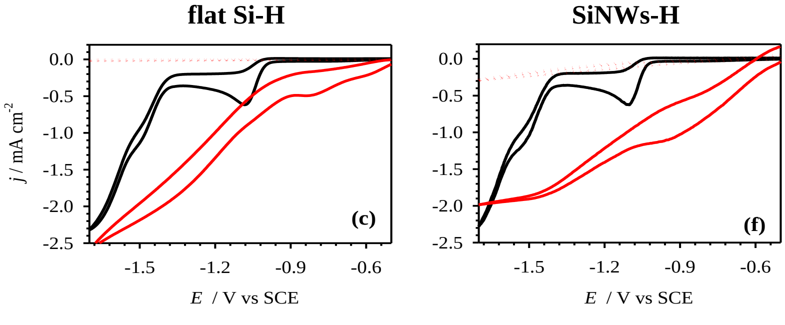
Proton-assisted multielectron reduction potentials for CO_2 lie within the bandgap of several semiconductors, in such a way that their use as photocathodes for this reaction allows a substantial decrease in the energy input required [1-3].

In the present work, hydrogen-terminated silicon nanowires (SiNWs-H) are used as a photocathode for the electrocatalytic reduction of CO_2 in the presence of different metallic bipyridyl complexes. Due to their nanostructured surface, SiNWs are highly interesting as light-harvesting electrodes, being efficient in converting solar to electrical energy, easy to make and stable under reduction conditions [4]. Among the tested complexes, we have used Mn non-noble metal based complexes to catalyze CO_2-to-CO photoelectroreduction, which is a less expensive approach versus the traditionally used based on rare and noble metal complexes [5].

The photoelectrochemical reduction of CO_2 at *p*-type SiNWs-H was achieved at potentials significantly lower than those required with a glassy carbon electrode (GCE) and planar Si-H [6]. Thus, for intermediate reduction potentials the photocurrent density values provided by silicon were noticeably higher than the current densities provided by GCE. Besides, impedance spectroscopic measurements were carried out and combined with cyclic voltammetry data to obtain the quantitative complete characterization of the energetics of all the systems studied. All the experiences were carried out at *p*-type flat silicon for comparison purposes and key electrocatalytic parameters such as fill factor (*FF*) and energy conversion efficiency (η) were determined.

Finally, in order to develop technologically viable electrocatalytic devices, the elaboration of SiNWs–H photoelectrodes modified with a Mn-based complex has been successfully achieved from an electropolymerizable catalyst, and it was shown that the electrocatalytic activity of the complex was retained after immobilization.





CVs of a solution of $[Mn(bpy)(CO)_3Br]$ at 1 mM in CH_3CN + 0.1 M Bu_4NClO_4 in the dark (dotted red lines) and under illumination through a red filter (solid red lines) under CO_2 + 5% v/v H_2O. Black lines: CVs obtained at GCE. v: 0.1 V s^{-1}.

[1] Aresta, M. et al., *Chem. Rev*. **2014**, *114*, 1709.
[2] Costentin, C. et al., *Chem. Soc. Rev.* **2013**, *42*, 2423.
[3] Schmidt-Mende, L. et al., *Angew. Chem. Int. Ed.* **2013**, *52*, 7372.
[4] Wang, D. et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 6709.
[5] Kubiak, C. P. et al., *J. Phys. Chem. C* **2010**, *114*, 14220.
[6] Torralba-Penalver, E. et al., *ACS Catal.* **2015**, *5*, 6138.

Nanostructure Design for Photocatalytic Water Splitting

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With their very high surface-to-volume ratio, the use of nanostructures is highly advantageous for photocatalytic water splitting. But next to their advantage of having a high surface-to-volume ratio, the physical properties of most semiconductors (absorption depth and charge carrier diffusion length) demand the use of one-dimensional nanostructures (e.g. nanowires, nanotubes and three-dimensional nanowire networks) to improve the transport of photogenerated charge carriers to the nanowire surface over the nanowire diameter (~ tens of nm), while maintaining optimal photon absorption over the nanowire length (~ tens of µm) [1-2].

In my past research and in my new group, the main focus lies on the investigation of these advantages gained by nano-engineering for photocatalytic water splitting considering several different nanostructures. Since templated electrodeposition is a very appropriate technique for designing different shapes of nanostructures with a wide choice of functionalities by materials selection, we use(d) this technique for the design of these different nanostructures for photocatalytic, photoelectrochemical and electrocatalytic water splitting. Among others, these nanostructures include:

- Multisegmented nanowires (ZnO|Ag, TiO_2/Ag) for autonomous photocatalytic water splitting [3-5],
- MoS_2 nanocube structures for electrocatalytic H_2 formation [6],
- p-Cu_2O nanocubes for photoelectrochemical water splitting [7],
- Mechanically stable and highly interconnected p-Cu2O and ZnO nanowire networks for photoelectro-chemical water splitting [8], and
- Metal Organic Framework (MOF) nanostructures, which are also expected to have many applications in (photo)catalysis [9].

Here, I will give an overview of these different photo- and electrocatalytic nanostructures and explain how they were made. In addition, I will also present their photo- or electrocatalytic activity, together with an explanation for their improved activity as compared to planar films of the same material.

References

[1] A. Sunkara *et al.*, *Catal. Today*, **199** (2013) 27-35.
[2] R. van de Krol *et al.*, *J. Mater. Chem.*, **18** (2008) 2311-2320.
[3] A. W. Maijenburg *et al.*, *J. Mater. Chem. A*, **2** (2014) 2311-2320.
[4] A. W. Maijenburg *et al.*, *J. Vis. Exp.*, **87** (2014) 51547.
[5] A. W. Maijenburg *et al*., *Small*, **7** (2011) 2709-1713.
[6] A. W. Maijenburg *et al*., *ACS Appl. Mater. Int.*, **6** (2014) 2003-2010.
[7] A. W. Maijenburg *et al*., *ACS Appl. Mater. Int.*, **5** (2013) 10938-10945.
[8] L. Movsesyan *et al., Semicond. Sci. Tech.*, **31** (2015) 014006.
[9] A. W. Maijenburg *et al*., *GSI Scientific Report* **2014** (2015) 270.

All-Inorganic Solar Synthesis of Liquid Formate from CO_2 and Water Over a Month on Durable and Recyclable Copper Iron Photocatalyst Films at Efficiency Exceeding Photosynthesis

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Harnessing and utilizing sunlight at high efficiency have represented an enormous challenge to the achievement of a carbon neutral society over the past four decades. Photocatalysis uniquely mimics natural photosynthesis in terms of light absorption and conversion, as well as storage of the absorbed photon energy into chemical bond energy. Despite this similarity, the development of low cost photocatalysts capable of selectively producing liquid chemicals from CO_2 and water with efficiency and durability comparable to those in typical photosynthesis remains a great challenge. Most of the photocatalyst suspension systems produce mixtures of gas and liquid products at poor efficiencies, whereas electrically biased film systems exhibit a near-commercial gas production efficiency, albeit only for disappointingly short periods. Herein, we report the facile, environmentally benign synthesis of $CuFeO_2$ and CuO binary films via electrodeposition, and demonstrate that these binary films produce only liquid formate from aqueous CO_2 at energy efficiency exceeding natural photosynthesis, while driving O_2 evolution from water on a wired Pt plate under continuous irradiation of simulated sunlight (AM 1.5G; 100 $mW{\cdot}cm^{-2}$) over 24 h. An as-synthesized photocatalyst film with a three-dimensional, double-layer configuration further shows the continued production of formate for over 17 days. However, the crystalline structure and elemental state of the used photocatalysts undergo gradual chemical reduction. Such a deformation can be thermally healed by recycling the weekly used samples via oxidative annealing. Thus, a single photocatalyst sample produces formate continuously for 35 days. The photocatalyst components (Cu, Fe, and O) are earth-abundant, and the photocatalyst synthesis is straightforward, facile, environmentally benign, reproducible, and scalable. On achieving higher efficiencies in the future, the practical applicability of these photocatalysts will become enormous.

Photoelectrochemistry of organic semiconducting polymers: fundamentals and implications in solar fuel generation

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The increasing atmospheric CO_2 levels in the last decades has drawn the attention to search for techniques which can efficiently convert this greenhouse gas into fuels and other useful chemicals. Photoelectrochemical (PEC) methods can be promising in this context, because they are easy to control, work under ambient conditions, and renewable solar energy is utilized to cover their energy demands. Up to now, mostly inorganic semiconductors (e.g., InP, GaAs, Cu_2O, $CuFeO_2$) have been applied as photocathodes in the PEC CO_2 reduction. There are several drawbacks (e.g., complicated synthesis procedures), however, which limit their large-scale applications. In contrast, there are only few reports on using organic semiconductors (conducting polymers, CP) as photocathodes in solar fuel generation.

The conduction band of conducting polymers lies above the thermodynamic potentials of the CO_2 reduction reactions, making the PEC reduction possible on these electrodes. Furthermore they can be easily synthesized either electrochemically or chemically under mild conditions. Finally, their physico-chemical properties can be simply tuned. All these factors together make them attractive photoelectrode materials for CO_2 reduction.

In my presentation I will report on the study of different electrodeposited CPs such as polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), polyindole in the PEC reduction of CO_2. Characterization of their photoelectrochemical properties, band structure, and product selectivity will be presented. As the CO_2 adsorption on the surface of the photoelectrodes can also play a key role in the reduction process, we have also investigated the adsorption characteristics of the polymer layers by quartz crystal microgravimetry and IR spectroscopy. By the systematic study of the polymers mentioned above, we established structure-performance relationships between the polymer structure and the PEC performance. By uniting that knowledge, we aim to design new CPs with more advantageous characteristics towards PEC CO_2 reduction (e.g., high CO_2 adsorption capacity, bandgap in the range of the visible light, long-term stability). For example, a CP consisting of alternating aniline and thiophene units (poly(4,2,-thyenilaniline)) has a notably reduced bandgap compared to polyaniline, while the amine groups ensure good CO_2 adsorption. Designing a CP with all the desired properties could open a new perspective in the PEC CO_2 reduction.

Support-Free-Titanium Oxynitride Nanocatalysts for Oxygen Reduction Reaction in Acidic Media

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Cathodic oxygen reduction reaction (ORR) is a rate-determining step in many fuel cells and air batteries. The ORR rate is particularly low in polymer electrolyte fuel cell (PEFC) cathodes, due to the low operating temperature of around 353 K and acidic environment in which pH is estimated to ≤ 1 [1]. Therefore, excessive amount of platinum-group-metal (PGM) catalysts have been employed to lower the overpotential. Although PEFC-powered vehicles and stationary power generation units have been commercialized in the last decade, the usage of PGM catalysts is still high for the widespread use [2,3].

Most of the non-PGM catalysts developed in the last decade contain iron, nitrogen, and carbon atoms [1,3,4] owing to the high activities. Most of the volume of this catalyst type, so-called Fe/N/C, is defective graphitic carbons which are degraded by corrosion during the startup/shut down to lose most of the activity [4]. We focused on another type of non-PGM catalyst—TiO_2 compounds—because they are insoluble in 0.1-mol dm^{-3} H_2SO_4 at 50°C for 24 days and are therefore stable in PEFC environments [5]. However, graphitic carbons such as carbon black [6–8], carbon nanotube [9], reduced graphene oxide [10,11] were still needed for insulating oxide-based catalysts to provide electronic paths to the oxygen defects which have been acknowledged as active sites [12]. These carbon materials should be protected from the corrosion and therefore situation is similar to that of carbon supported platinum or Fe/N/C catalysts. We therefore recently synthesized carbon-support-free titanium oxynitride (TiO_xN_y) catalysts with a conductive support, Ti_4O_7 [13]. The TiO_xN_y catalysts exhibited ca. 4 mA cm^{-2} of limiting current density and half-wave potential which is only 0.15 V lower than that of carbon-supported platinum in 0.1 mol dm^{-3} H_2SO_4 solution. However, the size was not well-controlled and the conductivity as well as surface area were still insufficient to result in the decrease in activity with increasing Nafion content in the catalyst layer.

In this work, the TiO_xN_y catalysts were synthesized without using supports. The surface elemental composition was well controlled to increase the reaction rate even with the use of Nafion ionomer. The mechanism will be discussed at the meeting.

Acknowledgments

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References

[1] F. Jaouen *et al.*, *ACS Appl. Mater. Interfaces*, **1**, 1623 (2009).
[2] T. Yoshida and K. Kojima, *ECS Interface* **24**, 45 (2015).
[3] J. P. Dodelet, Electrocatalysis in Fuel Cells, M. Shao (Ed.) p.271, Springer 2013.
[4] C. Choi *et al.*, *Angew. Chem. Int. Ed.*, **54**, 12753 (2015).
[5] J. H. Kim *et al.*, *Electrochim. Acta*, **52**, 2492 (2007).
[6] M. Chisaka *et al.*, *Electrochim. Acta*, **113**, 735 (2013).
[7] M. Chisaka *et al.*, *Electrochim. Acta*, **183**, 100 (2015).
[8] M. Chisaka *et al.*, *J. Mater Chem. A*, **4**, 2501 (2016).
[9] M. Chisaka *et al.*, *J. Mater Chem. A*, **3**, 16414 (2015).
[10] M. Chisaka *et al.*, *Phys. Chem. Chem. Phys.*, **16**, 20415 (2014).
[11] M. Chisaka *et al.*, *ChemElectroChem*, **1**, 544 (2014).
[12] M. Chisaka *et al.*, *Electrochim. Acta*, **88**, 697 (2013).
[13] M. Chisaka *et al.*, *Electrochim. Acta*, **214**, 165 (2016).

Co-axial Nanostructures for energy conversion: synergic effects between carbon nanotubes and metal oxide

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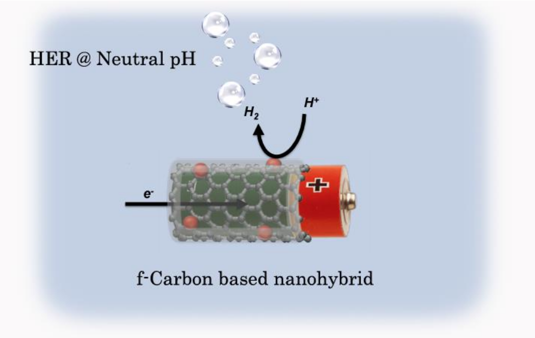
The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.[1] In particular a lot of efforts have been done in the field of chemical energy conversion, that remains very challenging because of the requirement for higher efficiencies.[2] The splitting of water to high energy chemical fuels is one of the most attractive and pursued alternatives; among the major issues there is the need to find catalytic systems that are able to boost the overall reaction efficiently and durably.[3]

In this context our group recently focused the attention on the study of catalytic systems for the oxygen evolution reaction (OER).[4] Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes (MWCNTs), metal oxides (TiO_2 and CeO_2) and Pd nanoparticles (Pd NPs).[5] The nanocomposites MWNT@Pd/TiO_2 and MWNT@Pd/CeO_2 have been designed and evaluated as electrocatalyst for the reaction of hydrogen evolution (HER) and for the CO_2 reduction, respectively.

Both systems exhibit very good performances and efficiencies, showing physical and chemical properties that differ to those expected from the simple sum of the individual building blocks. Due to these synergic effects, we shed light on the role of the MWCNTs in terms of their influence on the electronic properties of the two semiconductors (e.g. presence of surface states and different doping levels), resulting in better electrocatalytic activities.



References

[1] Armaroli, N.; Balzani, V. *Angew. Chem. Int. Ed.*, **2007**, *46*, 52-66.
[2] Centi, G. and S. Perathoner, *ChemSusChem*, **2010**, *3*, 195-208.
[3] Subbaraman, R.; Tripkovic, D.; Strmcnik, D.; Chang, K-C.; Uchimura, M.; Paulikas, A. P.; Stamenkovic, V.; Markovic, N. M. *Science,* **2011**, *334*, 1256-1260.
[4] Toma, F.; Sartorel, A.; Iurlo M. *et al., Nature Chemistry*, **2010,** *2*, 826-831.
[5] a) Mazzaro, R.; Boni, A.; Valenti G.; *et al.* **2015**, *4*, 268-273. b) Valenti, G.; Boni, A.; Cargnello, M.; *et al. Nature Communication DOI: 10.1038/ncomms13549*

Dynamic Photoelectrochemical Analysis of Photo-induced Electron Transfer at the Interface between Two Immiscible Electrolyte Solutions Functionalized with Photocatalytic Porphyrin Aggregates

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A photoactive assembly of photosensitizer aggregates at an electrified immiscible water-oil interface, often termed the *i*nterface between *t*wo *i*mmiscible *e*lectrolyte *s*olutions (ITIES), may achieve **incident-photon-to-current conversion without using solid electrodes to effect charge separation** by a process known as photo-induced heterogeneous electron transfer [1]. This flow of electrons from a hydrophobic redox species in the oil phase to a hydrophilic redox species in the water phase, *via* light excitation in the interfacial photoactive assembly, may be used to design a novel biphasic approach to solar energy conversion, as detailed in ***Fig. 1***.

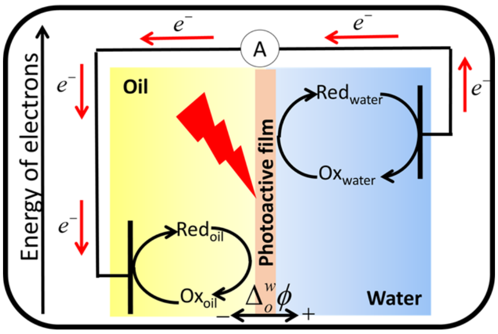

Fig. 1: *Scheme illustrating the concept that photoactive films trap solar energy, generating high-energy electrons. In theory this allows electron transfer across the interface between redox couples that thermodynamically are incapable of heterogeneous electron transfer in the dark due to their respective redox potentials in each phase.*

The basic design of all solar energy conversion devices necessitates **the efficient harvesting of light energy combined with an embedded asymmetry in the charge separation process**. The ITIES possess attributes to fulfil this remit including: (i) their ease of functionalisation with light harvesting photosensitizer molecules; and (ii) the separation of photoproducts on either side of the interface by local hydrophobicity gradients beneficially limiting unwanted recombination pathways to improve charge separation.

In this presentation, **the dynamics of the different charge transfer reactions (rates of electron transfer, photoproduct separation; *etc.*)** during the photo-induced heterogeneous electron transfer process at an ITIES functionalized with interfacial supramolecular assemblies of zinc tetrakis(4-carboxyphenyl) porphyrin (ZnTPPC) were studied by **intensity modulated photoelectron spectroscopy (IMPS)** [2-4], commonly applied to DSSCs.

These dynamic photoelectrochemical allow us to identify the precise experimental conditions required (in terms of interfacial aggregate surface coverage, aqueous phase pH, magnitude of the interfacial electrical polarization, etc.) to **maximise the photoconversion efficiencies possible at the ITIES** (currently unsatisfactorily < 1 %).

References

[1] Fermin, D.J. *et al., Chem. Commun.*, (1998), 1125.
[3] Fermin, D.J. *et al., Phys. Chem. Chem. Phys.*, (1999), ***1,*** 1461.
[3] Eugster, N. *et al., J. Phys. Chem. B.*, (2002), ***106,*** 3428.
[4] Eugster, N. *et al., J. Am. Chem. Soc.*, (2003), ***125,*** 4862.

Unprecedented Levels of Electrochemical Control over Photosensitizer Assembly at Soft Interfaces to Achieve Solar Fuel Generation without Solid Electrodes

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Common to all **solar energy conversion devices** are the abilities to harvest light and then separate the products of the photo-reaction, minimising recombination. Typically, charge separation takes place at the surface of nanostructured electrodes, often covered with photosensitizer molecules such as in dye-sensitized solar cells (DSSCs). However, the use of solid state architectures made from inorganic materials leads to high processing costs, occasionally the use of toxic materials and an inability to generate a large and significant source of energy due to manufacturing limitations [1].

Certain **soft interface**s formed between aqueous and organic electrolyte solutions of low miscibility (*e.g.*, trifluorotoluene) are **electrochemically active** in the sense that it is possible to precisely control the Galvani potential difference ($\Delta^w{}_o\phi$) between the two adjacent liquids (*i.e.*, to "polarise" or electrify the interface), and thus drive charge transfer reactions [2]. In comparison to solid electrode-electrolyte interfaces, where typically only electron transfer may be probed, charge transfer reactions at soft interfaces may include simple ion transfer, assisted ion transfer, heterogeneous electron transfer, or **photoinduced heterogeneous electron transfer** (PET, see ***Fig. 1***).

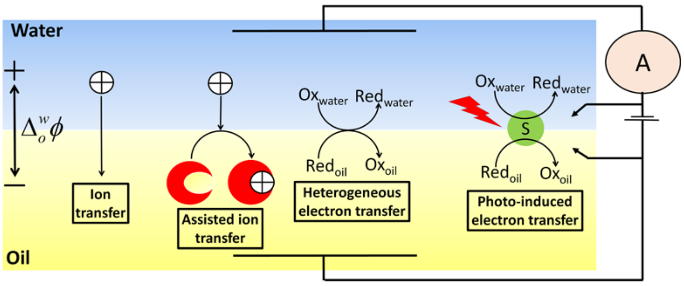

Fig. 1: *Summary of possible charge transfer reactions at polarised soft interfaces. A solar fuel such as H_2 or H_2O_2 may be generated at the soft interface via photo-induced electron transfer from a lipophilic electron donor in the oil phase.*

PET represents a novel method of potentially harnessing solar energy at electrified soft interfaces. By harnessing (i) energy trapped from visible light by the photoactive film (typically a porphyrin dye) and (ii) the electrochemical driving force provided by electrification of the soft interface, a **solar fuel** such as H_2 or H_2O_2 will be evolved by PET across the soft interface using a weak electron donor in the oil phase, *e.g.*, ferrocene (***Fig. 1***). Crucially, all photo-electrochemical techniques applied at traditional solid electrode-electrolyte interfaces (voltammetry, impedance, photo-current transients, *etc.*) are applicable at polarised soft interfaces [3].

In this presentation, **unprecedented levels of electrochemical control over photosensitiser assembly at soft interfaces will be presented, generating photoactive films with unique photophysical properties**. Photo-current transient data will be presented to demonstrate the feasibility of our goal to push the boundaries of the efficiencies of solar fuel generation at soft interfaces.

References

[1] Zweibel, K. *Science*, (2010), ***328,*** 699.
[2] Samec, Z. *Pure Appl. Chem.*, (2004), ***76,*** 2147.
[3] Fermín, D. J. *et al. J. Am. Chem. Soc.*, (1999), ***121,*** 10203.
[4] Halls, J. E. *et al. Energy Environ. Sci.*, (2012) ***5,*** 6541.

Ionic transfer triggered by light action: a case of TiO_2 nanocrystals towards photonic Li-ion battery

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Li-ion batteries need to be regularly recharged, thus being indirectly dependent on the systematic connection to the grid. On the other hand, photovoltaic (PV) systems application into day-to-day use is hindered by the intermittent nature of the sun power. Therefore, independent of the electrical infrastructure autonomous electrical energy sources are desired. As an alternative to conventional PV unit and battery coupling approach, a study on how ion transfer can be triggered subsequently to light absorption is herein proposed. This innovative approach, focusing on bi-functional semi-conducting electrode material combining electronic redox property and favorable crystal structure for ionic conduction, led to the demonstration of a photorechargeable half-cell lithium battery and non-intermittent PV device, thus closing the gap between electrochemical energy storage batteries and energy conversion photovoltaics.[1] This achievement was possible due to taking advantage of the two functions of material: sun energy conversion and energy storage by chemical means. The case of the n-type Li_xTiO_2 / TiO_2 nanocrystals will be herein discussed. The evolution of the opto-electronic properties and the dynamics of charge transfer in this system will be discussed on the basis of *in situ* / *in operando* experiments performed during the battery functioning based on both UV-Visible absorption spectroscopy and Time-Correlated Single Photon Counting (TCSPC).[2]

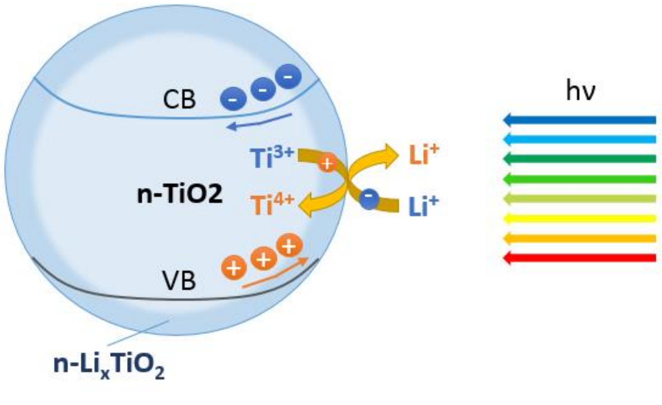

Figure 1. Schematic representation of the charge separation and Li^+ de-insertion processes in Li_xTiO_2 / TiO_2 nanocrystals under incident sunlight

[1] C. Andriamiadamanana, C. Laberty-Robert, F. Sauvage, CNRS-UPJV-UPMC, PCT/FR2014/053056
[2] C. Andriamiadamanana, I. Sagaidak, G. Bouteau, C. Davoisne, C. Laberty-Robert, F. Sauvage, submitted

Photoelectrocatalysis: Solar-assisted Hydrogen Production in Microgravity Environments

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Artificial photosynthesis systems, which follow the concept of the Z-scheme of natural photosynthesis, are presently being realized as catalyst-functionalized photovoltaic tandem devices for the photoelectrochemical oxidation of water and the simultaneous generation of hydrogen as a so-called "solar fuel". The successful implementation of an efficient photoelectrochemical (PEC) water splitting cell is not only a highly desirable approach to solving the energy challenge on earth: an effective air revitalization system generating a constant flux of O2 while simultaneously recycling CO2 and providing a sustainable fuel supply is also essential for the International Space Station and long-term space missions, where a regular resupply from earth is not possible.

Here, we present the photoelectrochemical production of hydrogen in microgravity environments on p-type indium phosphide electrodes with deposited rhodium electrocatalysts. Our findings indicate that microgravity has a significant impact on the gas bubble evolution behaviour and the mass transfer rate of the evolved hydrogen gas on the electrode surface. Furthermore, microgravity influences the current-voltage characteristics and the overall solar-to-hydrogen efficiency of the catalyst functionalized semiconductor-based half-cell. Further experiments with nanostructured rhodium catalysts fabricated by shadow nanosphere lithography on the InP surface suggest that the structure of the electrode surface plays a significant role for the gas bubble evolution behaviour and for the further the development of efficient prototypes for solar-assisted water splitting and hydrogen production that operate in micro- and hypergravity environments.

Enhanced Photoelectrochemical Efficiency of Self-Organized TiO_2 Nanotube Layers due to Secondary Materials

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The self-organized TiO_2 nanotube layers have attracted considerable scientific and technological interest over the past 10 years motivated for their possible range of applications including photo-catalysis, solar cells, hydrogen generation and biomedical uses [1]. The synthesis of 1D TiO_2 nanotube structure is carried out by a conventional electrochemical anodization of valve Ti metal sheet. The main drawback of TiO_2 is its applicability in the UV light (wavelengths < 390 nm). In order to enhance the efficiency, TiO_2 has been doped by N [2] or C [3] o to shift its absorption into the visible light.

Except of doping, one of the major issues to extend the functional range of nanotubes is to coat homogenously tube interiors by a secondary material. It has been shown that additional ultrathin surface coating of TiO_2 by secondary materials such as Al_2O_3 [4], ZnO [5] or MgO [6] annihilates electron traps at the TiO_2 surface and thus increases the photogenerated concentration of charge carriers. Recently, it has been demonstrated that just a single cycle of Al_2O_3 [7] or ZnO [5] deposited by atomic layer deposition (ALD) efficiently improve charge transport properties of the heterostructure while gradual passivation appears with increasing ZnO thickness due to stronger band-bending [5].

The presentation will focus in detail on the coating of the nanotube arrays by secondary materials using ALD. The deposited materials influence strongly photo-electrochemical properties of nanotube films. Experimental details and some very recent photocatalytic [8] and sensing [9] results will be presented and discussed.

References:

[1] J. M. Macak et al., *Curr. Opin. Solid State Mater. Sci.* 1-2 (2007) 3.

[2] C. Burda et al., *Nano Lett*. 3 (2003) 1049.

[3] S. Sakthivel et al., *Angew. Chem., Int. Ed.* 42 (2003) 4908.

[4] R. Zazpe et al., *Langmuir*, in press, DOI: 10.1021/acs.langmuir.6b03119.

[5] A. Ghobadi et al., *Scientific Reports* 6 (2016) 30587

[6] H. Park, et al., *Journal of Electroceramics* 23 (2009) 146.

[7] J-Y. Kim et al., *Nanotechnology* 25 (2014) 504003.

[8] M. Krbal et al., *Ms submitted.*

[9] S. Ng et al., *Ms in preparation.*

Molecular Photosensitizers: Emerging Sensing Tools

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Photoelectrochemical sensing is a rapidly emerging research topic. We show for the first time that molecular photosensitizers generating singlet oxygen, combined with electrochemical detection can efficiently replace enzymes in (bio)analytical applications, and thus overcome the drawbacks of current bioanalysis. Our photocatalytic systems, based on a fluorinated Zn phthalocyanine continuously form an easily detectable product under illumination so there is no need for additional compounds such as H_2O_2 to allow the detection. Thus, our strategy mimicks enzymatic systems, but being more robust and without the need to add compounds which might be chemically aggressive and unstable. The proposed system exhibits inherent baseline correction during on/off light cycles and is sensitive in the nano molar range, being able to selectively detect 20 nM amoxicillin in µL sample volumes. The fluorination of the sensitizer insures its long term stability and resilience vis-à-vis the reactive oxygen and other species it may generate. This new concept of a bioinspired strategy in which an enzyme is replaced by inorganic components for analytical purposes may find applications in many other (bio)analytical areas.

Ti/TiO_2 coated with Cu(II) aspirinate complex improved the photoelectrocatalytic reduction of CO_2 to methanol

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Abstract

The reduction of carbon dioxide emitted into the atmosphere has become a global pressing environmental challenge given its harmfully significant contribution to the greenhouse effect, which leads to global warming [1–3]. In this context, the photoconversion of CO_2 is a theme of high interest in artificial photosynthesis, where molecular species can be used to produce energy from sunlight, generating a useful fuel for storage and mobile use [4]. A novel copper (II) aspirinate complex easily deposited onto nanotubes of Ti/TiO_2 was successfully employed in the conversion of CO_2 to methanol through the use of UV-vis irradiation coupled to a bias potential of -0.35 V vs SCE. An average concentration of 0.8 mmol L^{-1} of methanol was obtained in 0.1 mol L^{-1} of sodium sulphate saturated with CO_2 using a self-organized Ti/TiO_2 nanotubular array electrode coated with $[Cu_2(asp)_4]$ complex. The results, we believe, may aid in enhancing the use of electron-mediating complexes when it comes to choosing photocatalysts for CO_2 reduction. The higher performance of the copper complexes associated with the photoelectrocatalytic technique may be attributed to a modification of the electronic features of the Cu(II) to Cu (I) in the complex, where electrons are promoted from the valence band to the conduction band when the semiconductor is irradiated. These electrons are found to easily reach the substrate surface while being trapped by Cu(II) in the complex which is simultaneously reduced to Cu(I). The complex acts as mediator enabling the indirect reduction of CO_2 to methanol and subsequent oxidation of Cu(I) to Cu(II) in the complex, concomitantly to the alcohol formation. Our findings, nonetheless, provide a meaningful contribution in the search for new materials integrating the Ti/TiO_2 nanotubes, which have been well explored in the literature, with economic, simple, easily obtained and stable copper complexes for the efficient conversion of CO_2 to an important fuel.

References

1. J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, Coordination Chemistry Reviews **255**, 1791 (2011).
2. N. S. Spinner, J. A. Vega, and W. E. Mustain, Catal Sci Technol **2**, 19 (2012).
3. S. A. Rackley, *Carbon Capture and Storage* (n.d.).
4. D. Gust, T. A. Moore, A. L. Moore, and G. Ciamician, Faraday Discuss **155**, 9 (2012).

Unique opto-electronic structure and photo reduction properties of sulfur doped lead chromates explaining their instability in paintings

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Chrome yellow refers to a group of synthetic inorganic pigments that became popular as an artist's material from the second quarter of the 19th century. The color of the pigment, in which the chromate ion acts as a chromophore, is related to its chemical composition ($PbCr_{1-x}S_xO_4$, with $0 \leq x \leq 0.8$) and crystalline structure (monoclinic/orthorhombic). Their shades range from the yellow-orange to the paler yellow tones with increasing sulfate amount. These pigments show remarkable signs of degradation after limited time periods. Pure $PbCrO_4$ (crocoite in its natural form) has a deep yellow color and is relatively stable, while the co-precipitate with lead sulfate ($PbCr_{1-x}S_xO_4$) has a paler shade and seems to degrade faster. This degradation is assumed to be related to the reduction of Cr(VI) to Cr(III). We show that on increasing the sulfur(S)-content in chrome yellow, the band gap increases. Typically, when increasing the band gap, one might assume that a decrease in photo activity is the result. However, the photo activity relative to the Cr content, and thus Cr reduction, of sulfur-rich $PbCr_{1-x}S_xO_4$ is found to be much higher compared to the sulfur-poor or non-doped lead chromates. This discrepancy can be explained by the evolution of the crystal and electronic structure as function of the sulfur content: first-principles density functional theory calculations show that both the absorption coefficient and reflection coefficients of the lead chromates change as a result of the sulfate doping in such a way that the generation of electron-hole pairs under illumination relative to the total Cr content increases. These changes in the material properties explain why paler shade yellow colors of this pigment are more prone to discoloration. The electronic structure calculations also demonstrate that lead chromate and its co-precipitates are p-type semiconductors, which explains the observed reduction reaction. As understanding this phenomenon is valuable in the field of cultural heritage, this study is the first joint action of photo-electrochemical measurements and first-principles calculations to approve the higher tendency of sulfur-rich lead chromates to darken. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Photoelectrochemical Charging of an Aqueous Flow Battery by a Polyaniline Surface-treated Hematite Photoanode

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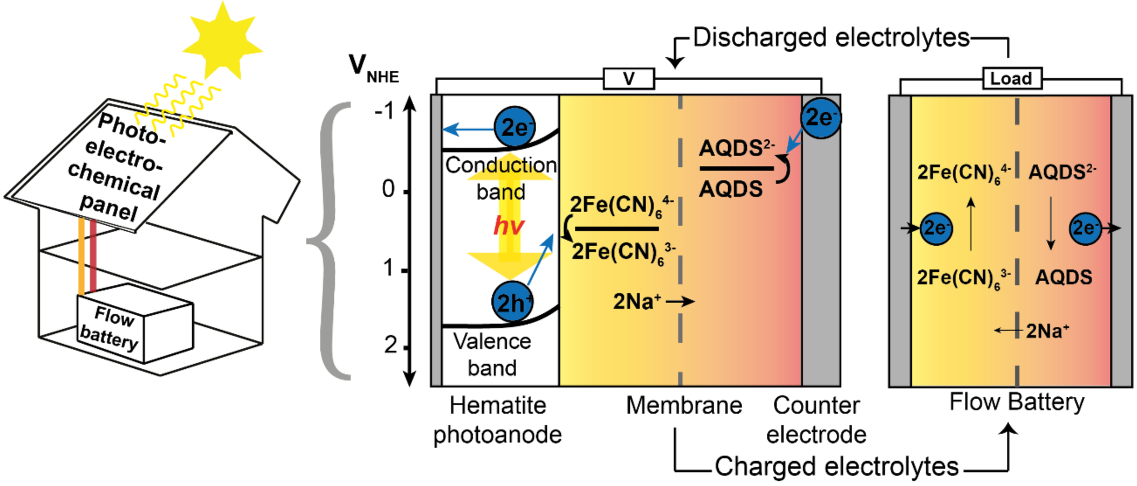
The intermittent nature of sunlight and the necessity for secure and sustainable energy sources drive research in energy storage technologies. In this work, direct solar charging of a 0.74 V flow battery with a surface modified hematite photoanode illustrates simultaneous photoelectrochemical harvesting and storage of solar energy using low cost and environmentally benign materials with high stability.[1]
The aqueous flow battery electrolytes consist of the metal complex ferrocyanide and the organic compound anthraquinone disulfonate (AQDS) dissolved in NaOH solution, while solar charging is facilitated by a thin-film (~ 40 nm) hematite (Fe_2O_3) photoanode.
The photoanode is made by spray-pyrolysis and subsequently surface treated with polyaniline (~ 10 nm) by electrodeposition and immersed directly in the ferrocyanide solution. Upon illumination of the photoanode-ferrocyanide interface, charge separation takes place in the hematite and photogenerated positive holes oxidize ferrocyanide while electrons reduce AQDS on the cathode, as illustrated in the figure below. The polyaniline layer increases the photovoltage of the junction by +100 mV and decreases the back-electron transfer recombination, as compared to bare hematite, which is a result of favorable energy-level alignment of the HOMO and LUMO levels of the polyaniline and the hematite band edges.
The photoelectrochemical charging process is unbiased up to 12 % state-of-charge of the battery, since the redox potentials of the ferrocyanide and AQDS redox reactions are within the bandgap of the photoanode, however, the AQDS redox potential lies close to the conduction band. Even though the unbiased photocurrent density shown is low (0.05 mA/cm^2), the stability of the system is high, and the photocurrent can be increased at least three times by employing an optimized cell design.
Photoelectrochemically charged redox flow batteries could be a promising technology given the varied material choices of semiconductors e.g. from the field of photoelectrochemical water splitting and of flow battery electrolytes within the growing field of especially organic redox-active species.

[1] Angew. Chem. Int. Ed. 2016, 55, 7142–7147



The envisioned end application of a solar redox flow battery as an energy-generation and storage system on household level and schematic illustration of the charging and discharging process in the presented system.

Photoelectrochemical reduction of CO_2 on organic/inorganic nanocomposite photoelectrodes

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The growing amount of carbon dioxide emission in parallel with the increasing greenhouse effect have put the utilization of carbon dioxide in the focus of scientific interest in the past decade. Photoelectrochemical (PEC) conversion of CO_2 is a thermodynamically uphill reaction, raising multiple requirements, which a good photoelectrode has to concurrently fulfill. Not surprisingly, as of yet, there is no single material which bears with all the necessary properties, thus there is a huge demand to develop new hybrid materials, which can be applied in this reaction.

We have demonstrated recently that beyond the traditional inorganic semiconductors (SCs), conducting polymers (CPs, e.g., polyaniline) can also be utilized for this purpose. At the same time polyaniline suffers from some handicaps, such as relatively small photocurrents and instability. Both of these can be traced back to the small charge carrier mobility, which results in extensive recombination. Carbon nanomaterials, especially carbon nanotubes and graphene (either alone, or as building blocks of organized 3D superstructures), are attractive candidates as large surface area electrode support materials. A viable way to overcome the small charge carrier mobility in CPs is to deposit the CP on a conducting nanonetwork, such as carbon nanotubes or graphene. This way the charge carrier pathway is decreased both to the current collector and to the electrode/electrolyte interface, which in turn results in higher currents and maybe different products that we experienced in the case of the bare CP.

In my presentation I will discuss the PEC behavior of polyaniline/ultra-long carbon nanotubes (ULMWCNT) and polyaniline/graphene nanohybrid photoelectrodes in the PEC reduction of CO_2 with various polymer/carbon ratios. The nanocarbons were spray-coated on to the electrode surface in all cases and the CPs were electrodeposited on these conducting nanonetworks. The composition of the nanocomposites was optimized in terms of both the thickness of the nanocarbon and the polymer layer. The morphology and the composition of the nanocomposites were characterized by SEM, TEM and Raman spectroscopy. The PEC behavior of the samples were investigated by linear sweep photovoltammetry and electrochemical impedance spectroscopy. One of the main goals of this study was to isolate the enhancement experienced in the measured photocurrents arising from the simple geometrical effects (both nanocarbon-modified electrodes has higher surface area compared to the bare substrate) from those corresponding to the effect of the nanocarbons on the charge carrier dynamics. Transient photocurrent measurements were also carried out for this purpose. The stability of the nanocomposite photoelectrodes was investigated by long-term chronoamperometric measurements along with the quantification of the formed products by GC-BID and GC-MS techniques.

Towards Wastewater Treatment: Photo-assisted Electrochemical Degradation of Nitrophenol and Orange II dye at a Tungsten Trioxide-Exfoliated Graphite Nanocomposite Electrode

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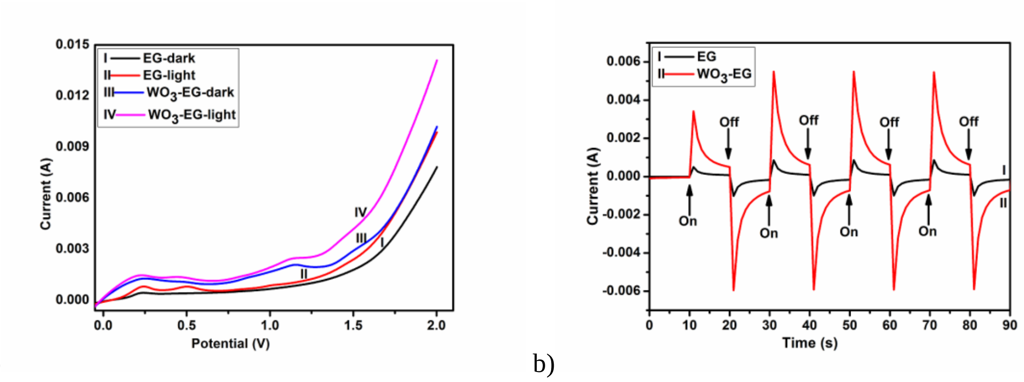
There is an ongoing quest for cheaper, efficient, solar responsive and novel electrochemical materials for the construction of electrodes used for electrochemical and photo-assisted electrochemical degradation (probably, mineralisation) of organics in wastewater treatment. In this regard a composite of tungsten trioxide (WO_3) and exfoliated graphite (EG) was synthesised, characterised, fabricated into a photoanode and employed in the electrochemical and photo-assisted electrochemical degradation of organic water pollutants. WO_3 nanoparticles were synthesised using a modified simple chemical method followed by calcinations at 600 °C. Then the composite was prepared by a wet chemical method after the exfoliation of the graphite. The WO_3-EG nanocomposite was characterised using voltammetry, X-ray diffractometry, Raman and FTIR spectroscopy, UV-Visible diffuse reflectance spectroscopy and scanning electron microscopy connected to energy dispersive X-ray spectrometry. The electrochemical and photo-assisted electrochemical applicability of the WO_3–EG as photo-electrode material was investigated by the degradation of 2-nitrophenol and orange II dye as model organic pollutants in a 0.1 M Na_2SO_4 solution, using a 10 $mAcm^{-2}$ current density. Photocurrent interrogations using white light from a xenon light source revealed that presence of WO_3 improved the photocurrent response of the EG-WO_3 nanocomposite electrode. Decolourisation and removal of the dye and 2-nitrophenol were monitored using a UV-Vis spectrophotometer and the mineralisation level was investigated using a TOC analyser. The EG-WO_3 nanocomposite electrode gave a higher degree of decolourisation (82% for 2-nitrophenol and 95% for orange II dye) and mineralisation (69% for 2-nitrophenol and 67% for orange II dye) in comparison to the EG electrode. Thus, this novel photoanode can be exploited for electrocatalytic applications (such as water treatment) under white light.



a) b)

Photocurrent responses of the nanocomposite electrode -Oriel LCA-100 Solar Simulator light source:
(a) Linear sweep voltammograms of EG and WO_3-EG composite electrodes with (light) and without (dark) xenon lamp; and (b) responses from photocurrent of EG ((I) black) and WO_3-EG ((II) red) composite electrodes in the dark (off) and under irradiation (on).

Controlling the Growth of Electropolymerized Polyaniline Nanorods through Vertically Oriented Silica Mesostructures

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Vertically oriented mesoporous silica films with narrow pore distribution around 2 nm can be generated by the electro-assisted self-assembly method (EASA)[1]. Such method allows the deposition of uniform mesoporous silica layer with the pores oriented normal to the electrode surface, subjected to the advantage of future functionalization of the pore walls and even taking advantage of the organized mesoporous structure as a hard template for the synthesis of nanostructured materials.

Conducting polymers (CP) have been known as materials with many promising applications in the field of energy storage, electroanalysis, electrochromic displays, photochemistry, etc. Among them, polyaniline (PANI) has been one of the most widely studied owing to its facile synthesis and environmental stability[2]. Above all the already existing asset of bulk PANI, its nanostructuration is considered to be interesting in order to enhance its electronic, optical and catalytic properties[3].

Based on the capacity of a vertically aligned mesoporous silica film to act as a hard template and to contribute to the mechanical strength of the CP–inorganic hybrid material[4], we have investigated the electropolymerization of aniline through such a film. It was conducted potentiostatically on the silica modified ITO electrode and the amount of deposited PANI can be controlled by the total number of charge transferred. Its growth within and beyond the silica template can be regulated with the aid of the particular shape of the amperogram. Moreover, the length of the one-dimensional nanostructured PANI could also be tuned by the thickness of the silica film.

The growth of PANI preferentially in the mesopores of the silica film was confirmed by electrochemistry, scanning and transmission electron microscopy (associated to EDS). Furthermore, the difference between the nanostructured and bulk deposited PANI was monitored using UV-vis spectroscopy and the improved capacitance of the PANI-silica/ITO electrode was verified by a charge-discharge experiment.

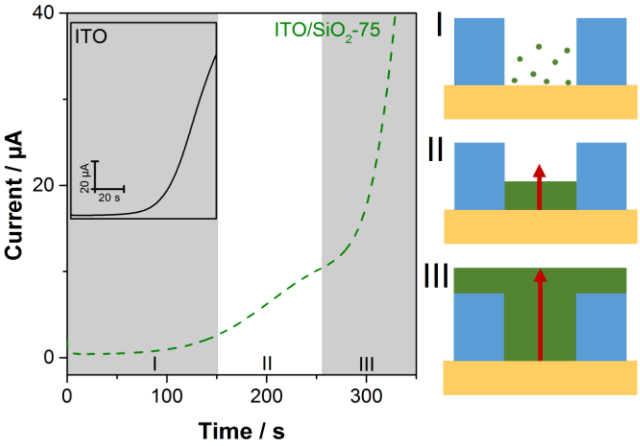

Figure 1: Potentiostatic electropolymerization of PANI at an ITO electrode modified with SiO_2-75 template (Q = 3mC). Inset: Electropolymerization at a bare ITO electrode (Q = 3 mC). (I) Induction and nucleation;(II) PANI nanowire formation within the mesochannels;(III) 3D PANI growth. The electrolyte solution was 0.5 M H_2SO_4.

1. Walcarius, A., Sibottier, E., Etienne, M. & Ghanbaja, J. Nat. Mater. 6, 602–608 (2007).
2. Dan, L. I., Huang, J. & Kaner, R. B. Acc. Chem. Res. 42, 135–145 (2009).
3. Yan, F., Lin, X. & Su, B. Analyst 141, 3482-3495 (2016).
4. Gamero-Quijano, A., Huerta, F., Salinas-Torres, D., Morallón, E. & Montilla, F. Electrochim. Acta 135, 114–120 (2014).

Effect of Applied Pressure on Photocatalytic Activity of Titanium Dioxide Synthesized by Cathodic Deposition with Supercritical Carbon Dioxide

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Supercritical fluid is any substance at a temperature and pressure above its critical point. Surface tension of supercritical fluid is extremely low and the physical properties can be easily adjusted by the pressure and the temperature. Hence application of supercritical CO_2 (sc-CO_2) in electrodeposition of materials is promising to overcome the problems encountered in continuous miniaturization of electronic components. However, CO_2 is non-polar and has very low electrical conductivity. Thus, a surfactant is used to form emulsions composed of an aqueous electrolyte, sc-CO_2, and the surfactant [1].

Materials electrodeposited with sc-CO_2 emulsified electrolyte (SCE) are reported to have properties very different from those electrodeposited by conventional methods. Grain refinement and surface smoothening are reported for Ni and Cu films electrodeposited with the SCE [1-3]. Grain size of the Ni electrodeposited with the SCE could be refined to be less than 10 nm [2]. Most interestingly, single crystal or twin crystal structure of Cu are observed when the SCE is applied in filling of Cu into the nano-vias [3].

TiO_2 obtained from cathodic deposition is usually amorphous. Therefore, an additional heat treatment process, such as 400ºC for 1 hr, is required to have crystalline TiO_2. This heat treatment process would increase the process time, and it could affect properties of the substrate and morphology of the TiO_2 films.

When the SCE is applied in cathodic deposition of TiO_2 films, deposited TiO_2 films are porous, and the films are composed of primary particles and aggregates of the primary particles [4]. In a recently study on cathodic deposition of TiO_2 films with the SCE, we found that crystallinity of the TiO_2 was significantly improved with increase of the applied pressure from atmospheric pressure to 35 MPa [5]. Anatase TiO_2 was obtained when the applied pressure was higher than 25 MPa without any additional heat treatment process. The effect of pressure on crystallinity of TiO_2 deposited is named hydrobaric effect, because the deposition mainly takes place in the aqueous phase in the emulsions and the effect is similar to the hydrothermal effect in some degree.

TiO_2 is known to have high photocatalytic activity, and the photocatalytic activity is affected by crystallinity of the TiO_2. Hence the hydrobaric effect is expected to affect the photocatalytic activity. In this study, photocurrent generated from the water splitting reaction using the as-deposited TiO_2 was evaluated. An increased in the photocurrent was observed for the TiO_2 deposited at a high applied pressure.

Reference:

[1] T.F.M. Chang, M. Sone, A. Shibata, C. Ishiyama and Y. Higo, *Electrochim. Acta,* **55** (2010) 6469.
[2] T. Nagoshi, T.F.M. Chang, S. Tatuo, M. Sone, *Microelectron. Eng*., **110** (2013) 270.
[3] N. Shinoda, T. Shimizu, T.F.M. Chang, A. Shibata, M. Sone, *Thin Solid Films*, **529** (2013) 29.
[4] T.F.M. Chang, W.H. Lin, Y.J. Hsu, C.Y. Chen, T.Sato, M. Sone, *Electrochem. Commun.*, **33** (2013) 68.
[5] W.H. Lin, C.Y. Chen, T.F.M. Chang*, Y.J. Hsu, M. Sone, *Electrochim. Acta*, **208** (2016) 244.

The Application of Photofuel Cells in Self-powered Sensing Platforms

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Since the Honda–Fujishima effect was reported in 1972, photocatalytic fuel cells (PFCs) have been extensively investigated in pollutant degradation, energy generation, hydrogen production, et al.[1,2] A typical PFC was fabricated on the basis of the concomitant processes of oxidation on photoanode and reduction on cathode, which could generate electrical power.[3] Nowadays, self-powered sensors have attracted considerable interest owing to their potential application in batteryless devices.[4] In our work, enzyme-free self-powered sensing platforms were proposed based on PFCs driven by visible-light, using glucose as model analyte.

Firstly, we constructed a glucose-air PFC using a $Ni(OH)_2/TiO_2$ photoanode and a Pt cathode in two chambers separated by a Nafion membrane, as illustrated in Figure 1A. Glucose was facilely photoelectrocatalytically oxidized in anodic chamber under visible light irradiation while dissolved oxygen was reduced in cathodic chamber. The polarization curves of cathode and photoanode were recorded to reveal the thermodynamic feasibility of the proposed PFC. The output performance of the proposed PFC was evaluated by the cell voltage to current (V-I) and power density to current (P-I) curves. It was found that the maximum output power density (P_{max}) of the PFC increased with increasing the concentration of glucose and a linear relationship was observed between P_{max} and logarithm of glucose concentration from 5 μM to 100 μM. To improve the self-powered sensing performance, we proposed a glucose-H_2O_2 PFC consisted of a $Ni(OH)_2/CdS/TiO_2$ photoanode and a hemin-graphene nanocomposite modified cathode. The CdS quantum dots on photoanode could improve the light absorption of photoanode and hemin-graphene was introduced to catalyze the reduction of H_2O_2 effectively. Compared to the aforementioned glucose-air PFC, such a glucose-H_2O_2 PFC exhibited a higher open circuit potential and output power density. Such a PFC was also employed in the self-powered sensing of glucose and it was found that the generated output power was sensitive to the variation of glucose concentration from 10 to 500 μM. The proposed self-powered sensing mechanism and the reaction of analyte on the photoanode were illustrated in Figure 1B. The proposed self-powered sensing methods based on PFC provided a novel way to the development of sensors without using external electrical power supply.

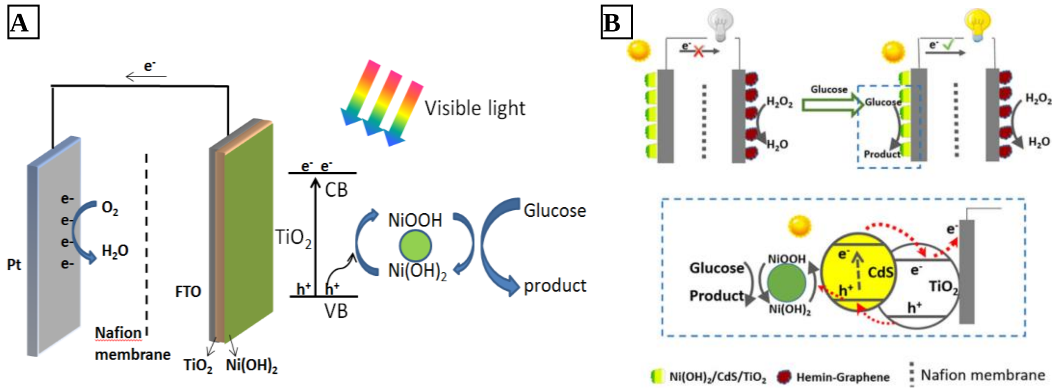

Figure 1. (A): Schematic illustration of visible light-driven PFC based on photocatalytic oxidation of glucose on $Ni(OH)_2/TiO_2$ photoanode. (B): Schematic illustration for the oroposed PFC based self-powered sensor and photoelectrocatalytic reaction of glucose on $Ni(OH)_2/CdS/TiO_2$ photoanode.

References
[1]. Ma, Y.; Wang, X.; Jia, Y.; et al. Chem. Rev. 2014, 114, 9987-10043.
[2]. Ravelli, D.; Dondi, D.; Fagnoni, M.; et al. Chem. Soc. Rev. 2009, 38, 1999-2011.
[3]. Lianos, P. J. Hazard. Mater. 2011, 185, 575-590.
[4]. Yan, K.; Yang, Y.; Okoth, O. K.; et al. Anal. Chem. 2016, 88, 6140-6144.

Dimensional, Interfacial, and Confinement effects on the Performance and Stability of Low-Cost Photoelectrodes for Solar Water Splitting

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The scientific community witnessed a considerable renewed interest in artificial photosynthesis for solar water splitting[1] within the last decade to address global pollution and climate change seriously compromising our environment and health as well as the concomitant exponential increase in energy demand from emerging countries.

Large bandgap transition metal oxide semiconductors offer a wide range of applications for solar energy conversion and renewable energy systems[2]. Most are stable, non toxic, earth-abundant, easy to prepare on a large scale from powders to thin films to ordered arrays at various dimensional scales. They do exhibit the widest range of optical and electronic properties required for low-cost solar water splitting applications.

Our approach is to develop novel purpose-built oxide heteronanostructures consisting of oriented arrays such as quantum rods sensitized Qdots of high purity entirely produced from aqueous chemical growth at low temperature[3] without surfactant nor template and with precise controlled size and interfacial chemistry[4] with intermediate bands for high visible-light energy conversion, highly quantized band structure for bandgap and optimized band edge[5] for stability against photocorrosion and operation conditions in aqueous solutions at neutral pH without sacrificial agent. Such unique characteristics, combined with the in-depth investigation of their size-dependent[6] and interfacial[7] electronic structure[8], optical, structural and conductivity[9] properties do provide a substantial advance in fundamental understanding as well as novel structure-efficiency relationships for a cost effective, efficient and sustainable generation of hydrogen from the two most abundant and geographically-balanced free resources on Earth, that is the sun and seawater.

All of the aforementioned will be demonstrated along with a new design strategy to hierarchically combine molecular and inorganic catalysts[10] as well as the latest development in heteronanostructured devices for low cost solar hydrogen generation[11] and atomic-scale fundamental understanding of the performance and stability of nitride photoelectrodes capable of overall water splitting in pure and seawater without applied bias[12].

References

[1] Y. Tachibana, L.Vayssieres, J. R. Durrant, *Nat. Photonics* **6**, 511 (2012)

[2] X. Kronawitter et al, *Energy Environ. Sci.* **7**, 3100 (2014); *Energy Environ. Sci.* **4**, 3889 (2011)

[3] L. Vayssieres, *Appl. Phys. A* **89**, 1 (2007); *Int. J. Nanotechnol*. **4**, 750 (2007); *Int. J. Nanotechnol.* **1**, 1 (2004); *Angew. Chem. Int. Ed.* **43**, 3666 (2004); *Adv. Mater.* **15**, 464 (2003); *J. Phys. Chem. B* **107**, 2623 (2003); *Nano Lett*. **2**, 1393 (2002); *Chem. Mater.* **13**, 4395 (2001); *Chem. Mater.* **13**, 233 (2001); *J. Phys. Chem. B* **105**, 3350 (2001); *Pure Appl. Chem.* **72**, 47 (2000)

[4] L. Vayssieres, *J. Phys. Chem. C* **113**, 4733 (2009); *Int. J. Nanotechnol*. **2**,411 (2005)

[5] *On Solar Hydrogen & Nanotechnology*, L. Vayssieres ed. (Wiley, 2010)

[6] L. Vayssieres et al, *Appl. Phys. Lett.* **99**, 183101 (2011); *Adv. Mater.* **17**, 2320 (2005)

[7] X. Kronawitter et al, *Nano Lett.* **11**, 3855 (2011); *Phys. Rev. B* **85**, 125109 (2012); *J. Phys. Chem. C* **116**, 22780 (2012)

[8] F. J. Himpsel et al, *J. Electron Spectrosc. Relat. Phenom.* 190, 2 (2013); C.X. Kronawitter et al, *PhysChemChemPhys* **15**, 13483 (2013); C. L. Dong et al, *Phys. Rev. B* **70**, 195325 (2004); J.H. Guo et al, *J. Phys. Condens. Matter* **14**, 6969 (2002)

[9] J. Engel et al, *Adv. Funct. Mater.* **24**, 4952 (2014)

[10] Y.K. Wei et al, *Nano Res.* **9**, 1561 (2016)

[11] J.Z. Su and L.Vayssieres, *ACS Energy Lett.* **1**, 121 (2016)

[12] M.G. Kibria et al, *Adv. Mater.* **28**, 8388 (2016)

Revealing Electronic Coupling in Semiconductor Nanoparticle Networks by Electrochemistry

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“Coupled organic-inorganic nanostructures (COINs) utilize organic semiconductors (OSCs) to facilitate charge carrier transport through nanocrystal (NC) ensembles by exploiting resonances in relevant energy levels between the NC and OSC.” [1]

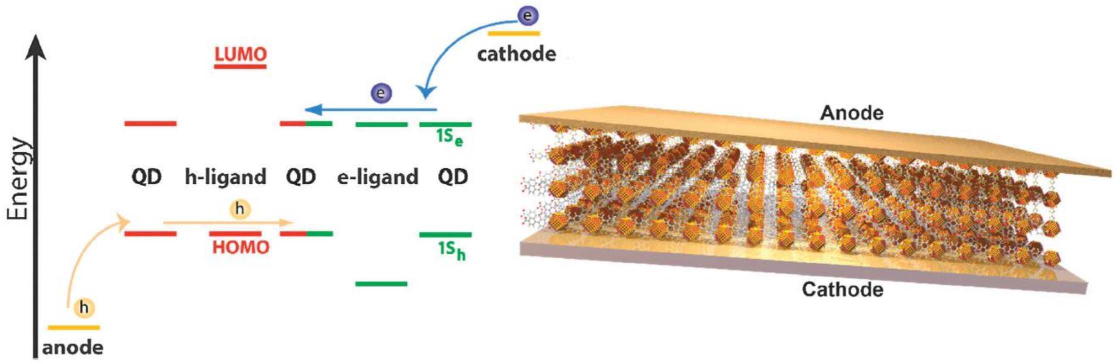

Fig. 1: Left: energy scheme of a COIN diode. Right: a diode composed of a COIN bilayer sandwiched in between an anode and a cathode.[4]

My work focuses on networks of PbS nanocrystals and phthalocyanine-derivatives and aims to find out about the position of the NC’s and OSC’s relevant energy levels and their alignment. UV-Vis-IR Spectroscopy, Electrochemistry, Spectroelectrochemistry as well as Potential Modulated Absorption Spectroscopy (EMAS) and In Situ Conductivity (ISC) are used in this research.
The findings will help to guide the engineering of energy level alignment in COINs, thereby reaching higher mobilities and increasing the performance of optoelectronic devices such as solar cells.

While the OSC can be easily characterized in solution with Electrochemistry and (thin layer) Spectroelectrochemistry, NC and COINs as solid state materials require a more sophisticated analysis.
The thickness of NC and COIN films is critical in a spectroelectrochemical experiment since a too thick film will be insufficiently charged by the surrounding electrolyte and a too thin film will not yield enough light absorption. EMAS uses potential modulation and login amplification to yield a high signal to noise ratio and thus allows to determine the conduction band edge of a thin NC film or COIN. [2]

After all band edges have been determined the critical question remains: will they couple electronically? ISC can be used to answer this question. It can also be applied to determine electron pathways within the film. [3]

The information gained from the methodologies above will enable a more efficient engineering of the components’ energy levels to produce optoelectronic devices like the one depicted in Fig. 1.

Literature:

[1] A. André et al., Chem. Mater., 2015, 27 (23), pp 8105–8115
[2] J. Poppe, S. G. Hickey and A. Eychmüller, J. Phys. Chem. C 2014, 118, 17123−17141
[3] B. L. Wehrenberg, D. Yu, J. Ma and P. Guyot-Sionnest, J. Phys. Chem. B 2005, 109, 20192-20199.
[4] M. Scheele, W. Brütting, F. Schreiber, Phys.Chem.Chem.Phys.,
2015, 17, 97.

Mask-Free Pattern for Solar Water Splitting and Biohybrid Electrode for CO_2 Reduction

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Producing commodity chemicals such as hydrogen and hydrocarbon products in eco-friendly manner is important to cope with the climate and environmental problems. In that sense, semiconductor based photoelectrochemical system for hydrogen production and various kind of catalysts for CO_2 reduction have been proposed and studied intensively over the past few decades. In this presentation, our own strategies for hydrogen evolution reaction (HER) and CO_2 reduction are introduced and discussed. First of all, we reported a mask-free metal patterning method which works based on the photoconductive nature of amorphous Si (a-Si) and the patterned light created by digital micromirror device. Ni-Mo, a non-noble metal electrocatalyst for HER, was directly patterned on a-Si by this method, and the Ni-Mo patterned a-Si photocathode showed moderate HER performance.1) Second, for the conversion of CO_2 to formate, formate dehydrogenase (FDH) and its cofactor NADH were immobilized together on the glassy carbon electrode with the electrochemically synthesized polydopamine (PDA) thin films. By incorporating this enzymatic biocatalytic cathode with cobalt phosphate/bismuth vanadate, a photoanode, we produced formate from CO_2 at highly efficient faradaic efficiency (>99%) without external bias and deterioration along at least one day.2)

1) Lee, Soo Youn, et al. "Light- Driven Highly Selective Conversion of CO_2 to Formate by Electrosynthesized Enzyme/Cofactor Thin Film Electrode." *Advanced Energy Materials* (2016).
2) Lim, Sung Yul, et al. "Light-guided electrodeposition of non-noble catalyst patterns for photoelectrochemical hydrogen evolution." *Energy & Environmental Science* 8.12 (2015): 3654-3662.

Electrochemically Structured Black Silicon for Water Oxidation

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The conversion of sunlight into storable and transportable chemical fuels, that can be used for generating electricity, is a very appealing alternative to batteries and could be highly beneficial to circumvent the intermittency of renewable sources of energy.[1] In this context, the development of photoelectrochemical cells (PECs) allowing the splitting of water for producing H_2 and O_2 at high rates is a very active field of research. Among all the semiconductors that have been studied for PECs, silicon (Si) is currently attracting a tremendous scientific interest for application in water splitting for several reasons.[2] First, it is the second most abundant element in the earth's crust and therefore is relatively cheap. Second, it has a narrow band gap of 1.1 eV, which is particularly adapted to the solar spectrum. However, Si suffers from two main drawbacks which are: its stability in aqueous media and its high reflectance.

In this contribution, we report a rapid, inexpensive two-step method for structuring *n*-type (100) Si surfaces with micron-sized cavities, the process is based on the photoelectrochemical etching (PEE) of the Si surface and its subsequent alkaline etching. This method produces a layer of random macropores over a large area, which renders the Si surfaces antireflective over the visible spectrum. We demonstrate that such surfaces can be conformably coated by anatase TiO_2 layers by atomic layer deposition (ALD) and that they can be used as stable photoanodes producing enhanced photocurrents under simulated sunlight with respect to their planar counterparts. These TiO_2-protected Si microstructured surfaces were highly stable in strongly alkaline solutions and were used as photoanode for several hours under simulated sunlight. Such photoanodes surfaces showed 50 % photocurrent enhancements and ~400 mV negative shift of onset potential without any co-catalysts, demonstrating their high potential for solar energy conversion applications.[3]

[1] N. S. Lewis and D. G. Nocera, Proc. Natl. Acad. Sci. 103, 15729 (2006).
[2] K. Sun, S. Shen, Y. Liang, P. E. Burrows, S. S. Mao, and D. Wang, Chem. Rev. 114, 8662 (2014).
[3] L. Santinacci, M. W. Diouf, M. K. S. Barr, B. Fabre, L. Joanny, F. Gouttefangeas, G. Loget, ACS Appl. Mater. Interfaces 8, 24810 (2016).

The Role of Anatase Surface Orientation in Selectivity of Photo-electrochemical Water Splitting

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Photo-electrochemical water splitting represents one of the key processes needed for successful utilization of renewable energy sources for distributed generation, storage and use of energy[1]. The research related to the electrochemical and photo-electrochemical splitting of water is primarily motivated by electricity storage in hydrogen. The overall process itself, however, is limited by the kinetically sluggish oxygen evolution reaction (OER). Primary effort was therefore focused on a development of new oxygen evolution catalysts based on rational design approach combining the DFT screening with target synthesis.

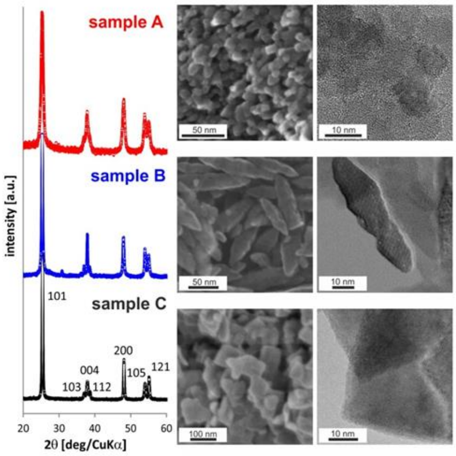

Figure 2 Powder X-ray diffraction patterns (left) and SEM images (middle) and HRTEM images (right) of anatase samples differing in the nanocrystal shape. The sample assignment is given in the Figure annotation. The SEM images were taken on the catalysts attached to the electrodes; the HRTEM images correspond to as prepared catalysts after calcination

This paper compares selectivity of three different types of anatase nanocrystals exposing different facets ({110}, {101} and {001}) (see Fig. 1) in photo-electrochemical water splitting. The fraction of conceivable reaction products was determined by means of on-line mass spectroscopic detection (DEMS). The {001} dominated surfaces apparently evolve over stoichiometric amounts of oxygen with respect to the passed charge. On the other hand, the {101} dominated surface evolve sub stoichiometric amount of oxygen with respect to passed charge while {110} featuring surfaces approach the situation when the MS detected amount of oxygen matches the passed charge assuming a four electron water oxidation process (see Fig. 2). The observed tendencies can be rationalized with help of the DFT calculation assuming the nanocrystalline electrode behaves electronically as macroscopic object [2] (i.e. the formation of SC layer is not hindered by the dimensions of the individual nanocrystals).

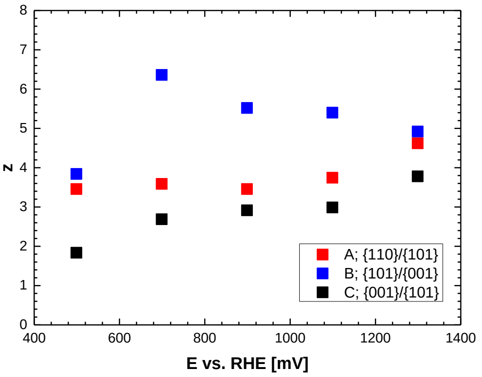

Figure 1 DEMS based average number of electrons needed to evolve one molecule of oxygen as a function of the applied potential on different anatase photocatalysts illuminated in acid (pH=1) electrolyte solution The sample colour coding is the same as in Figure 1.

[1] Lewis NS, Nocera DG, *Proc. Natl. Acad. Sci. U.S.A*, 103 (2006) 15729.
[2] Bisquert J, Garcia-Belmonte G, Fabregat-Santiago F, J. Solid State Electrochem., 3(1999) 337.

Molecular photoelectronics in Au/molecule/GaAs junctions

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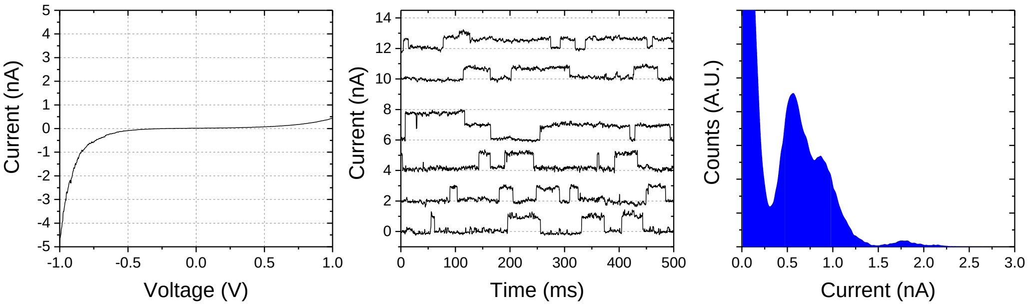
Organic monolayers on GaAs have been prepared previously as a way to modify the electronic properties of this technologically important surface, and the deposition of a metallic electrode on top of the monolayers allowed the study of charge transport through metal-molecule-semiconductor (MMS) devices.[1–3] Reducing the size of such devices to the single-molecule level is exceptionally attractive from a technological point of view, and the incorporation of a III-V direct bandgap semiconductor in a molecular junction is a significant expansion of the nanoelectronics "tool-box". Furthermore, the unique photoelectronic properties of GaAs could further expand its applications to the study of photoelectronic and photospintronic effects in MMS devices.

In conventional (large area) MMS devices the deposition of the metallic contact on top of the organic monolayer is a significant challenge[1,2], requiring utmost care in not damaging or altering the molecular structure. In our study we applied a technique commonly used to characterize metal-molecule-metal (MMM) junctions[4] to the "soft" fabrication of MMS nanodevices, In this technique, an Au STM tip is brought into contact with a dithiol passivating layer built on a GaAs substrate, and Au-S bonds spontaneously form, allowing the measurement of current-voltage characteristics through a small number (< 10) of molecules. Furthermore, by recording the current as a function of time, we can observe the stochastic formation and rupture of *single-molecule* junctions within the device, and therefore characterize their individual contributions to the overall current. The current-voltage characteristics of our nanodevices are remarkably similar to the ones observed in conventional MMS devices, and the current decay with length of an alkanedithiol series shows the same attenuation observed in MMM devices. Furthermore, by shining light on the GaAs substrate under reverse bias we are able to detect the generated photocurrent flowing through the device, and we found that the overall photocurrent flowing through the MMS junction is dependent on the choice of molecular bridge. We are now studying this phenomenon and our data suggests a dependence on the shape of the molecular resonances and their position relative to the semiconductor Fermi level. If this structure-property relationship proves to be reliable, it would allow further characterization of single-molecule junctions electrical properties and expands the possibility of designing functional MMS devices.



(left) Current-Voltage characteristics of a Au-molecule-GaAs device.
(centre) Current jumps attributed to the stochastic formation and rupture of single-molecule junctions.
(right) Histogram compiled from hundreds of individual current jumps, showing the statistical distribution of current values.

(1) Lodha, S.; Carpenter, P.; Janes, D. B. *J. Appl. Phys.* **2006**, *99* (2), 24510.
(2) Vilan, A.; Shanzer, A.; Cahen, D. *Nature* **2000**, *404* (6774), 166–168.
(3) Moons, E.; Bruening, M.; Shanzer, A.; Beier, J.; Cahen, D. *Synth. Met.* **1996**, *76* (1–3), 245–248.
(4) Haiss, W.; Nichols, R. J.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Schiffrin, D. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4330–4337.

Visible light active photoreactive hybrid layers with superhydrophobic properties

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In recent years, superhydrophobic surfaces with water contact angle (WCA) higher than 150° have received considerable attention due to their significant potential for practical applications ranging from self-cleaning surfaces. The second class of self-cleaning surfaces is photocatalytic coating which can chemically degrade organic materials when exposed to light [1,2]. During the photocatalytic process the irradiated photocatalyst particles produce highly reactive oxygen species and due to these formed reactive radicals the photocatalyst particles can degrade many organic compounds and inactivate microorganisms via destroying the cell wall and the DNA [1].

The main goal of our present work was to synthetized hybrid thin films with superhydrophobic and photoreactive dual properties. The plasmonic Ag-TiO_2 photocatalyst particles were shown photocatalytic properties under LED-light irradiation. The surface free energy of the visible light active hydrophilic Ag-TiO_2 photocatalyst particles was lowered by the using of a low energy fluoropolymer binder material. The prepared hybrid surfaces were shown not only photocatalytic but also superhydrophobic properties. The structure and morphology of the synthesised Ag-TiO_2 / fluoropolymer hybrid thin films were examined by SEM- measurements.

According to our experiments the structure of the thin films becomes more and more structured and roughened with the increasing Ag-TiO_2 nanocomposite content.

The surface wettability of Ag-TiO_2/fluoropolymer hybrid layers was determined by the measuring of water contact angle (WCA) values on the solid surfaces. The surface roughness of the low surface energy flat fluoropolymer layer was enhanced with the Ag-TiO_2 nanocomposite.

The photocatalytic activity of the prepared hybrid thin films were verified with ethanol photodegradation tests which was measured under LED light illumination (λ= 405 nm). The photooxidation measurements were determined by gas chromatography (Shimadzu GC-14B).

References

[1] Sz. P. Tallósy, L. Janovák, J. Ménesi et. al., *Environ Sci Pollut Res*, 21 (2014) 11155.
[2] Á. Veres, J. Ménei, L. Janovák, et. al., *Colloid Polym Sci*, 292 (2013) 207-217.

Silicon Photoanodes Stabilized by Electrodeposited Ni Nanoparticles

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Silicon is one of the most attractive materials for fabricating electrodes for photoelectrochemical cells because of its wide use in microelectronic and photovoltaic industries.[1] Moreover, it has a high carrier mobility, a suitable electronic structure and a band gap that allows absorbing all the solar spectrum.[1] Nevertheless, using Si as a photoanode material is very challenging since water oxidation is sluggish at Si surface and requires a substantial overpotential to occur and Si is highly prone to photocorrosion. Ni and NiO_x are excellent coating materials since they provide corrosion resistance and a high catalytic activity for the oxygen evolution reaction (OER) at high pH.[2] Several reports indicate that Ni layers, deposited by high vacuum techniques such as sputtering or evaporation can be used for protecting and enhancing the perfomances of Si photoanodes,[3] however, electrodeposition has not been used for this purpose so far.

We show here that Ni, electrodeposited on n-type Si from aqueous solutions, in the form of isolated or coalescent nanoparticles (NPs) protects the underlying and partially exposed Si from photocorrosion. Such photoanodes show a high photovoltage of ≈500 mV, state-of-the-art photocurrents and faradaic efficiencies >90 % under simulated sunlight at pH 14. Furthermore, these photoelectrodes are stable and can be operated at the light-limited catalytic current from 10 h to more than 40 h in 1 M NaOH. These findings demonstrate that robust and efficient Si photoanodes can be produced easily, which opens new opportunities for the implementation of low-cost Si-based monolithic photoelectrochemical cells for efficient solar fuel production.[4]

[1] a) K. Sun, S. Shen, Y. Liang, P. E. Burrows, S. S. Mao, and D. Wang, Chem. Rev. 114, 8662 (2014). b) N. S. Lewis and D. G. Nocera, Proc. Natl. Acad. Sci. 103, 15729 (2006).
[2] L. Trotochaud, J. K. Ranney, K. N. Williams, S. W. Boettcher, J. Am. Chem. Soc. 134, 17253 (2012).
[3] a) M. J. Kenney, M. Gong, Y. Li, J. Z. Wu, J. Feng, M. Lanza, H. Dai, Science 342, 836 (2013). b) K. Sun, M. T. McDowell, A. C. Nielander, S. Hu, M. R. Shaner, F. Yang, B. S. Brunschwig, N. S. Lewis J. Phys. Chem. Lett. 6, 592 (2015).
[4] G. Loget, B. Fabre, S. Fryars, C. Mériadec, S. Ababou-Girard, ACS Energy Lett. in press, DOI : 10.1021/acsenergylett.7b00034

Electro- and Photoelectrochemistry on TiO_2-based Nanorod Arrays via Anodizing Al/Ti and Al/TiN_x Layers

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Nowadays, many research efforts are dedicated to developing advanced materials for photoelectrochemical (PEC) splitting of water into oxygen and hydrogen. One of the materials investigated widely for this application is titanium dioxide. TiO_2 in the form of nanowire or nanorod arrays may lead to a substantial increase in the PEC activity compared with that of flat films due to the decoupling of the relatively long light penetration depth from the relatively short minority carrier pathway. On the other hand, critically small nanostructures may become in the flat-band condition, having no depletion layer necessary for effective charge carrier separation. Thus, an adjusted ratio of the nanorod size and its doping concentration leading to a depletion layer of an optimum thickness, occupying a big portion of the nanorod itself, may lead to charge separation taking place in a substantial portion of the nanorod volume, which is expected to increase the PEC response [1]. In this work, we report on the investigation of various types of crystallinity, oxygen vacancy concentration, and nitrogen doping level in the TiO_2-based nanorod arrays prepared via porous-anodic-alumina (PAA)-assisted anodization of Ti and TiN_x films in order to adjust the depletion layer thickness to take up substantial volume of the nanorods. To evaluate semiconductive properties of the nanostructures, we perform electrochemical impedance spectroscopy (EIS) measurements at various potentials in the dark on differently fabricated and modified TiO_2 nanostructures. Also we correlate the properties of differently prepared TiO_2 nanoarrays with the preliminary results of their PEC water splitting performance.

TiO_2-based nanorod arrays are prepared by anodizing of Al/Ti [2] or Al/TiN_x precursor layers in an oxalic-acid-based electrolyte [3] (Figure 1). The Al layer is anodized at 40 V to form PAA; then the Ti or TiN_x layer is re-anodized to 100 V. This leads to the growth of titania or N-containing titania nanorods within the alumina pores, being approx. 40 nm wide and 160 nm long. Subsequently, some samples are annealed in air or vacuum at 600°C to modify the crystallinity and oxygen vacancy concentration. Finally, the surrounding PAA may be partially or completely etched to vary the extent to which the nanorods protrude from the alumina overlayer, to expose their surface for the PEC reaction.

Cyclic voltammetry and EIS measurements were performed at different potentials in a borate buffer solution with and without the presence of Fe^{2+}/Fe^{3+} redox couple in the dark. The Mott-Schottky analysis revealed an increase in the depletion layer capacitance with decreasing the potential, which is in agreement with *n*-type doping of the TiO_2 nanorods. Besides, the calculated donor density varied with the annealing conditions and with the nitrogen content, which allows for tuning the thickness of the depletion layer and thus enhancing the charge carrier separation during PEC water splitting.

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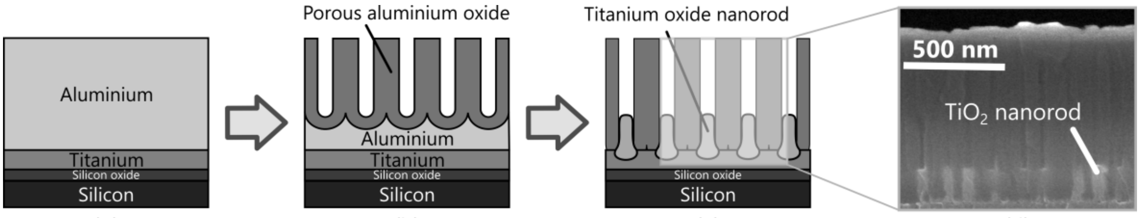

Figure 1. (a–c) Schematics of PAA-assisted anodizing of an Al/Ti bilayer leading to the formation of PAA-embedded TiO_2 nanorod array. (d) Cross-sectional SEM image of N-containing TiO_2 nanorods.

[1] M. Bendova, F. Gispert-Guirado, A. W. Hassel, E. Llobet, A. Mozalev, Nano Energy 2017, in press, doi: 10.1016/j.nanoen.2017.01.029.

[2] R. M. Vázquez, R. Calavia, E. Llobet, F. Guirado, J. Hubálek, A. Mozalev, Procedia Engineering 2012, 47, 833.

[3] A. Mozalev, M. Sakairi, I. Saeki, H. Takahashi, Electrochim. Acta 2003, 48, 3155.

Carbon materials/α-Fe_2O_3 electrodes: Synthesis, characterization and application in photoelectrocatalysis.

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The photoelectrocatalysis has been widely studied its efficiency in the removal of organic contaminants in the until reaching the mineralization of these pollutants. The hematite (α-Fe_2O_3) is a semiconductor considered promising for this process. α-Fe_2O_3, n-type semiconductor, has a band-gap energy of 2.2 eV (visible light region).[1] Its photocatalytic activity is diminished by some factors, such as particle size or defects in its structure and its low conductivity. The carbonaceous materials show an important role in the improvement of this semiconductor photocatalytic activity. These serve as support for the semiconductor particles and decrease the recombination of the e^-/h^+ pair. The following materials were used: graphite, carbon black (CB), carbon nanotube (CNT) and exfoliated graphene (EG). These materials were added to the hematite precursor and synthesized by a hydrothermal route and then calcined at 600 ° C.[2] Materials were characterized by several structural techniques, such as DRX, TGA/DTA, MEV, Raman, among others. The films were deposited on glass plates coated with conductive layer (ITO) by the Layer by Layer (LbL) technique with 1 and 4 layers. Besides, the films were characterized by electrochemical techniques, such as cyclic voltammetry and chronoamperometry. The photoelectrochemical profiles electrodes showed an augmentation in photocurrent with potential increasing, during the anodic scan, characteristic of n-type semiconductor. Moreover, photocurrent density was higher for all tested electrodes with light irradiation when compared with electrochemical process at dark, Table 1. The film composed by 4 layers of Fe_2O_3/CNT presented the highest photocurrent with an approximate value of 1.93 μA/cm^2. The photocatalytic activity of these synthesized materials was tested in photooxidation of methylene blue, following the pseudo-first order kinect. All electrodes synthesized with the carbon materials presents better results than the pure hematite electrodes and, as expected, which greater the number of layers, increased the photocalytic efficiency, Table 1. The electrode that presented the best catalytic activity in the discoloration of the methylene blue was the one containing 4 layers of Fe_2O_3/EG with approximately 70 % of its initial decolorization. Photocatalysis was held to be proven its inefficiency against photoelectrocatalysis. The discoloration in photocatalysis was 25% for hematite calcined at 600 ºC. This shows that the junction of electrochemical and photochemical techniques improve the efficiency of a catalytic material. This is due to the motion of the excited electron from the semiconductor to be transported to the counter electrode while the hole generated form radicals OH• to oxidize organic molecules.

Table 1. Variation of current density (Δj) obtained for electrodes synthesized with different layers at +1.3 V (KCl 0.1M) with and without irradiation of visible light, electroactive area (A), the rate constant (k_{obs}) of degradation of the dye and percent discoloration of methylene blue at +1.1 V.

Layers/ Electrode	Δj / (μA/cm^2)	A / (cm^2)	k_{obs} / (x10^{-3}min^{-1})	R^2	% discol.
1 – Fe_2O_3	0.10	1.18	3.57	0.980	35
1 – Fe_2O_3/graphite	0.11	1.12	3.85	0.984	43
1 – Fe_2O_3/CB	0.07	1.03	3.77	0.986	40
1 – Fe_2O_3/CNT	0.22	1.36	4.01	0.992	47
1 – Fe_2O_3/EG	0.25	1.34	3.98	0.975	46
4 – Fe_2O_3	0.12	1.76	6.74	0.972	53
4 – Fe_2O_3/graphite	0.31	1.19	6.95	0.994	59
4 – Fe_2O_3/CB	0.47	1.33	7.04	0.990	62
4 – Fe_2O_3/CNT	0.73	1.93	9.10	0.991	68
4 – Fe_2O_3/EG	0.71	1.85	9.25	0.985	72

References

1. D. Wang, Q. Wang, T. Wang. Nanotech. 22 (2011) 135604.
2. L. C. Ferraz, W. Carvalho Jr., D. Criado, F. L. Souza. Appl. Matter. And Interf. 4 (2012) 5515.

The influence of surface states on the photocatalytic reduction processes

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The electronic structure of a semiconducting material strongly influences its chemical properties. It determines the progress of photogeneration, separation, transportation and recombination of charge carriers. In recent years an increasing number of publications on heterogeneous photocatalysis appeared, describing numerous semiconductors acting as photocatalysts. More and more sophisticated materials have been designed and engineered to facilitate various photocatalytic processes. The activity of all of them is governed by interfacial redox reactions, which involve electrons and holes as reducing and oxidizing agents. Since the efficiencies of these processes depend on a variety of factors, (such as accessibility of the adsorbed reactants and charges, the lifetimes and energies of the latter) the accurate characterization of electronic structures of photocatalysts seems crucial.

In recent years there have been several attempts to design techniques for characterization of semiconductor electronic structures, mainly for nanomaterials.[1,2] We propose a modified spectroelectrochemical method as a new technique to characterize the electronic states localized close to the edge of the conduction band.[3] Distribution of additional electronic states localized within the bandgap can be qualitatively and quantitatively characterized using this approach. The applicability of our method, in determination of deep and shallow electron traps was confirmed for selected semiconductors such as titanium dioxide, zinc oxide and zinc sulphide.

The proposed method has been applied to determine the influence of the surface states localized within the bandgap on the photocatalytic processes such as carbon dioxide, oxygen and water reduction. Correlations between efficiencies of those reactions and electronic structures will be presented and discussed.

Acknowledgements

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References

[1] M. Jankulovska, T. Berger, T. Lana-Villarreal, R. Gómez, Electrochim. Acta 62, 172-180 (2012)
[2] D. Mandal, T. W. Hamann Phys. Chem. Chem. Phys., 17, 11156-11160 (2015)
[3] M. Kobielusz, K. Pilarczyk, E. Świętek, K. Szaciłowski, W. Macyk, in preparation

Synthesis and structural investigation of tungsten oxynitride and tungsten nitride nanostructures

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Tungsten nitrides and oxynitrides are promising materials due to the wide variety of potential applications in methanol oxidation[1], electrochemical[2] and photoelectrochemical hydrogen evolution[3] and it can be used as an electrode in other electrochemical devices due to the good chemical stability, high strength, hardness, and high melting point with good electrical conductivity and a relative low band gap energy[4].

In our study, hydrothermally synthesized tungsten oxide nanowire were heat-treated in ammonia/nitrogen atmosphere at different temperatures, in order to produce tungsten oxynitride and tungsten nitride. Changes in the structures and the electrochemical properties of the nanowires were investigated, and subsequently compared to that of samples treated in inert nitrogen atmosphere. The alteration in the morphology and structure of the samples were studied with transmission and scanning electron microscopy (TEM, SEM), and electron and X-Ray Diffraction techniques (ED, XRD). Band positions were determined by photoelectrochemical measurements.

X-ray diffraction results showed, that the pristine tungsten oxide nanowires were transformed into tungsten oxynitride and tungsten nitride due to the high-temperature calcination steps in ammonia atmosphere. Electronmicroscopy images revealed, that in paralell with the phase transformation above, the initial fibrous WO_3 morphology was gradually converted into nanosheets. Band gap energies of the treated samples were significantly decreased in the calcination processes.

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[1] Shibin Yin, Lixiang Yang, Lin Luo, Fei Huang, Yinghuai Qiang, Hongwei Zhang, Zaoxue Yan, NewJ.Chem., 37 (2013), 3976.

[2] Jinle Shi, Zonghua Pu, Qian Liu, Abdullah M. Asiri, Jianming Hua, Xuping Sun, Electrochim Acta 154 (2015) 345–351

[3] Vidhya Chakrapani, Jyothish Thangala, Mahendra K. Sunkara, Int. J. Hydrogen Energy 34 (2009) 9050 – 9059

[4] L. Villasecaa,n, B.Morenoa, I.Loritea,b, J.R.Juradoa,c, E.Chinarroa, Ceram. Int 41 (2015) 4282–4288

Structural and Morphological Characterization of Semiconductor Hybrid Thin Films with Tunable Wetting Properties

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Superhydrophobic surfaces, with a liquid contact angle θ greater than 150°, have important practical applications. It is known in the literature that many efforts have been made to develop an artificial superhydrophobic surface by mimicking the lotus leaf structure [1]. In general, to create a superhydrophobic surface, are needed a surface with low energy and a surface roughness.

The second class of self-cleaning surfaces is photocatalytic coating which can chemically degrade organic materials when exposed to light, a process known as “photocatalysis” [2, 3]. Due to the surface hydroxylation, the measured contact angle of the semiconductor thin films is closed to the zero value and that means superhydrophilic wetting properties. For the purposes of practical application it is very important to attach the semiconductor photocatalyst particles to a solid surface. The different polymeric or macromolecular materials are highly suitable for this application.

The main goal of our present work was to synthetized semiconductor thin films with tunable wetting properties from superhydrophobicity to superhydrophilicity ($0° < \theta < 150°$). The hybrid thin film consist of hydrophilic photocatalyst particles and polymer binder materials with different chemical structure and solubility. The surface roughness and wetting properties of the two component hybrid layers were gently adjustable by the photocatalyst particle/ polymer ratio. Moreover, at ideal surface roughness (particle/ polymer ratio) the wetting properties of thin films were also adjustable with the polymer hydrophilicity. According to the photocatalytic measurements the layers were shown not only photoreactive but also superhydrophobic properties. The thin films were prepared by simply spray- coating method which is a low-cost, fast and large-scale film- forming technique. This dual superhydrophobic and photoreactive coatings with selective surface wetting properties are very attractive in different applications.

References

[1] Á Deák, L. Janovák et. al. Applied Surface Science 389 (2016) 294.
[2] Sz. P. Tallósy, L. Janovák, J. Ménesi et. al., Environ Sci Pollut Res, 21 (2014) 11155.
[3] Á. Veres, T. Rica, L. Janovák, et. al., Catalysis Today, 181 (2012) 156.

Electrochemical, photoelectrochemical and microelectrogravimetric characterization of two- and one-dimensional cuprous thiocyanate films electrochemically deposited in aqueous media

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Cuprous thiocyanate (CuSCN) has a key role in photovoltaics as hole transporting layer (HTL) in new solid state solar cells. Other semiconductors used as electron transporting layers in these devices, such as ZnO and TiO_2, can be electrochemically deposited with controllable morphology from thin films to nanostructures. CuSCN probably is among the few inorganic p-type semiconductors that belong to this list, which can be electrodeposited in aqueous solutions showing two- and one-dimensional structures. The aqueous electrolyte employed for this process is composed by $CuSO_4$ with additives (TEA and EDTA) [1] and the substrates employed were FTO-coated glass and ITO-coated quartz (for eqcm studies). Thus, both morphologies have been studied by capacitance (EIS), photocurrent and microelectrogravimetric (eqcm) measurements. Morphology and structural features of samples were obtained from SEM, TEM and XRD studies. Capacitance measurements revealed the p-type character of both kinds of morphologies, considering the effective area obtained from SEM analysis. Photocurrent measurements showed a tendency towards square-wave behavior of photocurrent-time responses indicating no-recombination of minority carriers [2], whereas the magnitude of the measured photocurrent in one-dimensional CuSCN was evidently higher than in the two-dimensional ones. Eqcm analysis gives support to the hypothesis that the participation of the aqueous species CuH_2Y (Y: fully deprotonated EDTA) and colloidal $Cu(SCN)_2$ is critical in the variation of the diameters of the one-dimensional CuSCN structures [3]. In addition, the Faradaic efficiency for both kinds of CuSCN structures was only slightly lower than the theoretical value, thus proving the scalability of this process when applied in photovoltaics. TEM analysis revealed the one-dimensional CuSCN structure is polycrystalline, thus ruling out a growth mechanism similar to the ZnO single crystal nanowires also grown by electrochemical deposition [4]. The two-dimensional CuSCN prepared by this method has been reported as both good seed and blocking layer in solar cells, whereas one-dimensional CuSCN can be electrochemically grown on these seed layers in order to complete the whole HTL in these solar cells [5].

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References

[1] D. Ramírez, K. Álvarez, G. Riveros, B. González, E. A. Dalchiele, Electrodeposition of CuSCN seed layers and nanowires: A microelectrogravimetric approach, *under submission*.
[2] L. M. Peter, Dynamic Aspects of Semiconductor Photoelectrochemistry, Chem. Rev. 90 (1990) 753.
[3] C. Chappaz-Gillot, R. Salazar, S. Berson, V. Ivanova, Insights into CuSCN nanowire electrodeposition on flexible substrates, Electrochim. Acta 110 (2013) 375–381.
[4] S. P. Anthony, J. I. Lee, J. K. Kim, Tuning optical band gap of vertically aligned ZnO nanowire arrays grown by homoeptaxial electrodeposition, Appl. Phys. Lett. 90 (2007) 103107.
[5] C. Chappaz-Gillot, S. Berson, R. Salazar, B. Lechêne, D. Aldakov, V. Delaye, S. Guillerez, V. Ivanova, Polymer solar cells with electrodeposited CuSCN nanowires as new efficient hole transporting layer, Sol. Energ. Mat. Sol. Cells 120 (2014) 163–167.

Nanorod Electrodes of CdS and CdSe for Photoelectrochemistry

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Hydrogen is a clean and renewable energy that can be produced by the photoelectrochemical (PEC) water splitting method. It is also a method to store solar energy. The technology has been extensively studied during the past several decades, but cost-effective engineering devices has not been realized yet. The critical issues in the development are bandgap engineering of the photoelectrode semiconductors, good quality nonepitaxial materials synthesis, and photo-corrosion, etc. Therefore, solid understanding of the semiconductor-semiconductor and semiconductor-electrolyte interfaces is necessary. We fabricated 3-D nano-structural PEC electrodes towards high photocurrent density and conversion efficiency based on TiO_2 nanorod template. CdS and/or CdSe overlays were taken as the main light-absorbing materials. Our focus was made in measurement and discussion of the band-diagram in the PEC system for solid understanding of the PEC process. We fabricated CdS/CdSe photoanode nano-structures showing a high performance of current density ~20 mA/cm^2 and conversion efficiencies >10%, and discussed the PEC process. The voltage measurements between the three electrodes and their analysis were carried out towards band alignment at the semiconductor-electrolyte interface.

Nanostructured CuI/PbI_2 Alloys Act as Highly Efficient Photoelectrodes for Nitrate Reduction

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One of the greatest challenges of this century is to consume environmentally friendly energy instead of the conventional non-renewable ones. The largest renewable energy source is the sunlight, which might be harnessed using the knowledge gained in the field of photoelectrochemistry in the past 30 years.

Photoelectrodes can utilize solar energy in several ways: solar energy is either converted into electricity, or stored in the form of chemical energy. This strategy includes photoelectrochemical (PEC) hydrogen evolution and PEC carbon dioxide reduction into useful fuels. A further possible application of PEC methods is environmental remediation that reduces heavy metals as well as other harmful ions, or oxidizes hazardous organic compounds.

There are multiple requirements that a photoelectrode must comply with: it has to be (1) stable, (2) insoluble in the test medium, (3) resistant to photocorrosion; but in the meantime, it is expected to (4) have a broad optical excitation regime, and (5) to show good charge separation-, and transfer behavior, etc. One single material, however, cannot meet all these criteria. For this reason, composite materials are often considered, which contain several different components. These components are selected according to their individual task, for example, being a co-catalyst, or responsible for photo-absorption, etc. Design and synthesis of an effective composite photoelectrode material is a major enterprise – hence, it has become one of the main research projects in the field of photoelectrochemistry.

In this study, we investigated CuI/PbI_2 composite system in the PEC reduction of nitrate ions. Lead iodide and its derivatives (e.g., hybrid organic–inorganic perovskite systems) have excellent absorption properties in the visible light range, efficient charge carrier separation, and good charge carrier transport behavior. These materials, however, are sensitive to water (dissolve in water), which greatly hinders their application. On the contrary, copper(I) iodide is not a water-soluble compound; it has a wide bandgap; consequently, it is an UV light-excitable material. The 1:1 mixture of lead and copper iodide forms a eutectic point that we utilized on preparing the photoelectrodes. Thus, CuI/PbI_2 composite was deposited on the ITO glass electrode using the thin film melting technique. As a result, hexagonal lead iodide crystals formed with copper iodide nanoparticles on their surface. Then, we investigated the PEC reduction of nitrate ions, and the operation of the CuI/PbI_2 composite material as a photoelectrode. A number of structural characterization methods and different photoelectrochemical techniques were performed. The products formed were determined by ion chromatography and UV-vis spectrophotometry.

These results show that the CuI/PbI_2 composite nearly three times more efficiently reduces the nitrate ions on exposure to light, than the pure substances. This improvement is originated from the corresponding bandgap positions of the components: photogenerated electrons can easily transfer from lead iodide particles onto copper iodide nanoparticles. It helps the charge separation, hence, the electrons (from copper iodide) more easily reduce the nitrate ions. Preliminary results reveal that nitrate ions are converted into nitrite ions and nitrogen gas, but it is expected that under appropriate conditions the reduction will proceed until ammonium ions form in the solution.

The investigated CuI/PbI_2 system illustrates the operation of a well-designed composite photoelectrode. A similar, but more environmentally friendly system might be used for reducing nitrate and nitrite ion content of waste water with the aid of solar energy.

Conducting Polymer or Biological System Based Mixed Junctions for Photoelectrochemical Reduction of Carbon Dioxide to Alternative Fuels

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A gradual decline of energy resources induces interest in new energy systems. Driving the conversion of CO_2 with sunlight allows for storage of solar energy in the form of carbon-based chemicals. What is more, oxide semiconductor materials can be used to perform such energy transformation.

Global warming and transformation of light energy into usable, chemical energy justify the wide interest in reducing carbon dioxide. According to the above-mentioned arguments, the purpose of our research project is development and characterization of mixed system capable of photoelectrochemical reduction of carbon dioxide. We have been able to drive effectively photoelectrochemical reduction of carbon dioxide through hybrid system composed of p-type semiconductor and conducting polymer (polyaniline) or biological component (a strain of Yersinia enterocolitica). A meaningful point was the stabilization of p-type semiconductor – Cu_2O with respect to anodic photocorrosion. Conducting polymers have drawn significant interest of researchers because of their extraordinary properties such as electrical characteristics, controllable chemical and electrochemical properties and according to our research mainly due to it resistance to (photo)corrosion. The results obtained with photoelectrochemical reduction of CO_2 showed that the polymer layer reduces the corrosion rate. Moreover, it was found that mechanical, partial damage of the conducting polymer layer have no significant influence on the recorded current densities.

Counterfactual attempt to protect copper(I) oxide surface without diminishing performance of photoelectrochemical reduction of carbon dioxide may refer to utilization of biological systems. Whole cell biocatalysts and microbial electrocatalysts have been considered to use. Microorganisms can form very stable biofilms well-adhering to different solid surfaces. Modern scientific reports have shown that bacterial biofilms have electrocatalytic properties and have the ability to exchange electrons with the electrode surface.

Transition Metal Complexes for Catalytic Electroreduction of Carbon Dioxide

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The catalytic reductive transformation of carbon dioxide (CO_2) to fuels and commodity chemicals is one of the most important contemporary energy and environmental challenges. Since CO_2 is very stable, the direct electroreduction of CO_2 into CO requires high potential. Numerous homogeneous and heterogeneous catalysts have been reported for electrochemical CO_2 reduction.

Our goal was to demonstrate that palladium nanocenters can be generated within the coordination architecture of tridentate Schiff-base-ligands by electrodeposition from the supramolecular complex of palladium(II), $[Pd(C_{14}H_{12}N_2O_3)Cl_2]_2 \cdot MeOH$. The resulting Pd nanoparticles are stabilized and activated by nitrogen coordination sites, and the electrocatalytic system exhibits appreciable activity toward reduction carbon oxide (IV) in 0.1 mol dm^{-3} $KHCO_3$. The catalytic activity of CO_2 reduction was estimated from the oxidation charge of the adsorbed products. The adsorbed products obviously interferes with the formation of the oxide film on the Pd surface. CO is one of the important products generated in CO_2 electroreduction. Electroactive products, such as carbon monoxide was detected by using classical electrochemical methods.

It is well known that the catalytic performance of metal complex catalysts for CO_2 reduction strongly depends on the chemical properties of the metal center and ligand. It is expected that the distribution of the products, the current efficiencies, and the reaction mechanism of CO_2 electroreduction will also be affected by the type of central metals and ligands in complexes.

The reduction products in homogeneous reactions, have been limited to CO and HCOOH. The aim of the present study was to construct a homogeneous reaction system capable of multi-electron reduction of CO_2. Ruthenium complexes have certain characteristics that make them attractive as potential electrocatalysts for CO_2 reduction. Our laboratory has developed and studied the use of water-soluble iminophosphorane ruthenium (II) compounds. These systems will also be considered for functionalization of photoelectrochemically active semiconducting metal oxides.

Bacterial Biofilm with Metal Nanoparticles and their Complexes: New Approach toward Enhancement of Reduction of Carbon Dioxide

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The interest in the electrocatalytic reduction of carbon dioxide is constantly growing, and researchers are in the need of applying the process of binding carbon to synthetic fuels production. CO_2 molecule is known for its stability, and its electroreduction is characterized by large over-potentials: consequently selective and efficient electrocatalysts are needed. One of the challenges during the process is competing with simultaneous hydrogen evolution; the role of hydrogen reaction pathway is significant in CO_2 electrocatalytic reduction selectivity and dynamics. [1]

Metallic catalysts and their complexes (e.g. Cu, Pd, Pt) are commonly used in the electrocatalytic reduction of carbon dioxide. Recently, alternatives for efficient CO_2 electroreduction include utilization of biological systems, even microbial electrocatalysts, in which microorganism often occur in a form of bacterial biofilms. Biofilms form very stable layers composed of microbes well-adhering to various surfaces. [2] There is a huge differentiation in microbial metabolic pathways, because of the different types of enzymes in microbial cell, and that creates the opportunity to catalyze many redox processes at ambient conditions, also carbon dioxide electroreduction. [3] Bacterial biofilm hydrated structure also allow water molecules to easily move through it, and in electrochemical measurements it permits aqueous electrolyte to flow undisrupted at the electrocatalytic interface. It is needed to improve the electrical connection between microbes and electrode surface, and one of the ideas is the utilization of highly porous conductive polymers (such as polyaniline or polypyrrole), which also facilitate immobilization of the bacterial cells. They are well known as surface modifiers for immobilization of different nanoparticles. Recently, bioelectrochemical systems often use also carbon nanotubes together with biological layers due to their capabilities of penetrating microbial structures and improving the overall conductivity. These properties are particularly important in developing biosensors and microbial fuel cells.

We propose here a hybrid multilayered matrix, composed of polyaniline-supported *Yersinia enterocolitica* biofilm, multi-walled carbon nanotubes (MWCNTs) and dispersed Pt nanoparticles (nPt) on the top. The underlayer of polymer, biofilm and MWCNTs has been demonstrated to work as highly active assistance for nPt during carbon dioxide electroreduction in neutral electrolyte (phosphate buffer at pH=6.1). Application of the hybrid system allows clear distinction of the CO_2-reduction currents from those originating from the hydrogen evolution, unlike the bare nPt dispersed at glassy carbon surface. The result complies with the enhancement effect toward process of carbon dioxide reduction rather than hydrogen evolution. [4]

Bacterial biofilms are increasingly being used in electroreduction of carbon dioxide, [4,5] as well as in the photoelectrocatalytic reduction of this compound [6]. Furthermore, the structure and properties of microbial matrix enable the possibility of immobilization of different nanoparticles in the film, stabilization of photoelectrochemically active semiconducting materials, as well as the possibility of decorating biofilms with various reactive compounds.

[1] Anna Wadas et al., *Electrocatalysis*, 2014, *5*, 229
[2] A. Alissandratos, H.-K. Kim, C. J. Easton, *Bioresource Technol*, 2014, *164*, 7
[3] S. Freguia, T. Tsujimura, K. Kano, *Electrochimica Acta*, 2010, *2*, 813
[4] Ewelina Seta et al., *Australian Journal of Chemistry*, 2016, 69 (4) 411-418.
[5] Hyojin Hwang et al., Bioresource Technology 185 (2015) 35-39
[6] Xiaoxin Cao et al., Energy & Environmental Science 2 (2009) 498-501

Determination of synergic effect of nitrogen and boron as dopants precursors of TiO_2 nanotubes according to its photoelectrochemical answer under visible light.

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Obtaining photoanodes based on TiO_2, which are appropriate for use in photoelectrocatalytic processes and are photosensitive to wavelength in visible range, it is an important aspect of study. The preparation of electrodes based on TiO_2 nanotubes and co-doped with nitrogen and boron (N, B/NT- TiO_2/Ti) is proposed as an alternative to extend absorption range of TiO_2 from UV region to other of less energy (visible region) and to improve photoanswer of co-doped TiO_2 nanotubes in comparison to TiO_2 nanotubes without doping (NT- TiO_2/Ti) or monodoped with nitrogen (N/NT- TiO_2/Ti) or boron (B/NT- TiO_2/Ti). The synergic effect of boron and nitrogen under visible light was evaluated through measurements of open-circuit potential (OCP), Linear sweep voltammetry (LSV), cyclic sweep voltammetry (CV) and impedance spectroscopy, using a three electrodes cell, a graphite bar as counterelectrode, an electrode of Ag/AgCl (3 M KCl) as a reference electrode and the photoelectrodes of NT- TiO_2/Ti, N/NT- TiO_2/Ti, B/NT- TiO_2/Ti y N, B/NT- TiO_2/Ti with an area of 1 cm^2 as working electrodes. The study was carried out using a solution of 0.1 M of sodium sulphate (Na_2SO_4). Under the conditions described was possible to demonstrate a synergic effect between boron and nitrogen, because of improving of photoelectrochemical properties and high photocurrent density using N, B/NT- TiO_2/Ti as a work electrodes in comparison to monodoped TiO_2 nanotubes and TiO_2 nanotubes without any kind of modification.

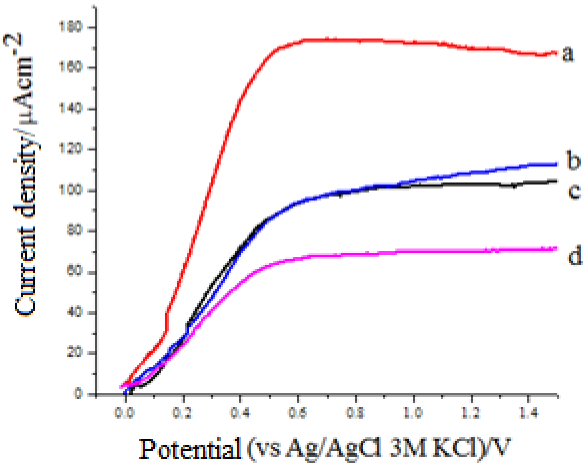

Fig. 1. Linear sweep Voltammery of TiO_2 nanotubes (codoped y mono-doped) obtained using a sweep speed of 100 mVs^{-1} of a) N, B/NT-TiO_2/Ti, b) N/NT-TiO_2/Ti, c) B/NT-TiO_2/Ti y d) NT-TiO_2/Ti. Electrolyte: 0.1 M Na_2SO_4 a pH 7.

Photoelectrochemical Oxidation of Methanol on Pt/TiO$_2$/Glucose Doped Carbon

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Despite the high potential of direct methanol fuel cells (DMFCs) due to the advantages of using a liquid fuel such as methanol, the electrooxidation of methanol (MOR) on Pt is slow under ambient conditions due to the adsorption of reaction intermediates that result in a rapid deactivation of the Pt catalyst nanoparticles.[1-2] Several metal oxides, mainly TiO$_2$, have been studied as alternative co-catalysts for Pt because of their unique co-catalytic activity that can be enhanced under UV illumination.[3-4] In this study, a method based on the use of glucose as a carbon modifier (GDC) has been implemented to prepare TiO$_2$/GDC nanostructured substrates for Pt nanoparticles.[5-6] Electrochemical characterization experiments have shown the as prepared Pt/TiO$_2$/GDC materials had a higher catalytic activity and stability toward the methanol oxidation reaction (MOR) and better resistance to CO poisoning compared with in-house fabricated Pt/C. Under UV-visible illumination, MOR activities on Pt/TiO2/GDC were nearly 2.3 times higher than that of Pt/C, which indicated that its electrocatalytic and photocatalytic properties had been integrated to boost the catalytic performance for MOR.

References

1. Qian W., Wilkinson, D. P., Shen J., Wang H., Zhang J. (2006). J. Power Sources, 154(1), 202-213.
2. Fukunaga H., Ishida T., Teranishi N., Arai C., Yamada K. (2004). Electrochim. Acta, 49(13), 2123-2129.
3. Wang Y. Q., Wei Z. D., Gao B., Qi X. Q., Li L., Zhang Q., Xia M. R. (2011). J. Power Sources, 196(3), 1132-1135.
4. Ohtani B., Prieto-Mahaney O. O., Li D., Abe R. (2010). J. Photochem. Photobiol. A: Chemistry, 216(2), 179-182.
5. Odetola C., Easton E. B., Trevani L. (2016). Int. J. Hydrogen Energy, 41(19), 8199-8208.
6. Odetola C., Trevani L., Easton E. B. (2015). J. Power Sources, 294, 254-263.

Electrochemical Modification of Bismuth Sulfide Films

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Thin films of bismuth sulfide show promise for application as photovoltaic converters, optoelectronic and thermoelectric devices, and photodiode arrays. In the present study bismuth sulfide was formed using the successive ionic layer adsorption and reaction (SILAR) method. The electrochemical modification of bismuth sulfide films with cobalt was carried out in the Co^{2+}-containing electrolytes at different pH values. The resulting cobalt modified bismuth sulfide film surfaces were characterized by X-ray photoelectron spectroscopy and scanning electron microscopy.

It has been determined that the bismuth sulfide film initiates the reduction of Co^{2+} ions prior to the traditional overpotential deposition of it. The processes occurring during the reduction of bismuth sulfide film in the Co^{2+}-containing electrolyte depend on the electroreduction medium. At pH 5 it occurs at more negative potential values and the rate of cobalt electrodeposition on the bismuth sulfide surface was greater than that at solution pH 3. The XPS analysis confirms the incorporation of cobalt into the bismuth sulfide film during the reduction of bismuth sulfide film in the Co^{2+} containing solution at pH 3 and 5: both on the film surface and at a film depth of 2 nm cobalt and cobalt oxy/hydroxy compounds were detected.

The proposed method can be applied for the cobalt electrodeposition on dielectrics, using thin bismuth sulfide films as an activator.

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Investigation of Kinetics of Electroless Deposition of Cobalt Using Titanium Ion Redox System

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In recent years electroless metal deposition is widely used for metallization of various dielectrics, fabrication of mirrors, galvanoplastic, formation of catalysts used in fuel cells, fabrication of microcircuit, optoelectronic, etc. An efficiently strong reducing agent is required for autocatalytic metal deposition. The use of traditional reducing agents (formaldehyde, borohydride, hypophosphite, etc.) is limited due to simultaneously occurred the parasitic reactions with the oxidation of reducing agent: the deposited coatings have a structure with large defects. In the present study the reducing agent – titanium ion redox system (Ti^{3+}/Ti^{4+}) was used for electroless deposition of cobalt (Co) layers on the copper (Cu) surface, which allows to solve this problem.

Kinetics of electroless deposition of Co layers on the Cu surface using Ti^{3+}/Ti^{4+} as a reducing agent has been investigated by means of electrochemical quartz crystal microgravimetry (EQCM) under stationary and hydrodynamic conditions. Influence of plating solution pH on the rate of Co deposition was also investigated.

It was found that the rate of electroless Co deposition depends on solution pH as well as on hydrodynamic conditions. The highest deposition rate of Co (40 µg cm^{-2} min^{-1}) has been obtained when the electroless Co deposition was carried out at hydrodynamic conditions and pH of the electroless Co plating solution was ca. 8.8.

It should be noted that the Co layers deposited on the surface of Cu using Ti^{3+}/Ti^{4+} redox pair as a reducing agent were continuous and compact.

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Photoelectrochemical Activity of Bi_3YO_6

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Bismuth based photocatalysts *e.g.* $BiVO_4$ [1], $Bi_4V_2O_{11}$ [2], Bi_2WO_6 [3], BiOCl [4], Bi_2MoO_6 [5] and others attract great attention due to the promising photocatalytical properties. Among them, bismuth vanadate exhibits outstanding photoactivity under visible light illumination. However, $BiVO_4$ is characterized by low mobility of charge carriers that results in high rate of e^-/h^+ recombination [6]. Thus, great effort has been taken to find other Bi-containing compounds that exhibit higher photoactivity due to *i.a.* the inhibition of adverse recombination process. One of them, Bi_3YO_6 has not been characterized as potential photocatalyst yet, however structure, electrical and ionic conductivity of Bi_3YO_6 have been studied [7,8].

In this study, Bi_3YO_6 was synthesized *via* conventional solid state reaction technique using appropriate amounts of Bi_2O_3 and Y_2O_3. Optical properties of material was examined using UV-vis spectroscopy technique, both in transmission and reflectance mode. Obtained pale yellow powder was deposited onto FTO substrate and FTO/Bi_3YO_6 electrodes were electrochemically tested in three-compartment cell. Electrochemical impedance spectroscopy and cyclic voltammetry techniques were applied to examine electrochemical properties of Bi_3YO_6 layers in contact with aqueous electrolyte. Chronoamperometry curves collected in the dark and under simulated solar light illumination were recorded in order to measure photocurrent.

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References

[1] K. Trzciński, M. Szkoda, K. Siuzdak, M. Sawczak, A. Lisowska-Oleksiak, Enhanced photoelectrochemical performance of inorganic–organic hybrid consisting of $BiVO_4$ and PEDOT:PSS, Appl. Surf. Sci. 388 (2016) 753. doi:10.1016/j.apsusc.2016.02.143.

[2] K. Trzciński, A. Borowska-Centkowska, M. Sawczak, A. Lisowska-Oleksiak, Photoelectrochemical properties of BIMEVOX (ME=Cu, Zn, Mn) electrodes in contact with aqueous electrolyte, Solid State Ionics. 271 (2015) 63. doi:10.1016/j.ssi.2014.10.008.

[3] J. Sheng, X. Li, Y. Xu, Generation of H_2O_2 and OH Radicals on Bi_2WO_6 for Phenol Degradation under Visible Light, ACS Catal. 4 (2014) 732–737. doi:10.1021/cs400927w.

[4] L. Ye, L. Zan, L. Tian, T. Peng, J. Zhang, The {001} facets-dependent high photoactivity of BiOCl nanosheets, Chem. Commun. 47 (2011) 6951–6953. doi:10.1039/c1cc11015b.

[5] G. Tian, Y. Chen, W. Zhou, K. Pan, Y. Dong, C. Tian, et al., Facile solvothermal synthesis of hierarchical flower-like Bi_2MoO_6 hollow spheres as high performance visible-light driven photocatalysts, J. Mater. Chem. 21 (2011) 887–892. doi:10.1039/C0JM03040F.

[6] F.F. Abdi, T.J. Savenije, M.M. May, B. Dam, R. Van De Krol, The Origin of Slow Carrier Transport in BiVO 4 Thin Film Photoanodes :, J. Phys. Chem. Lett. 4 (2013) 2752.

[7] I. Abrahams, X. Liu, S. Hull, S.T. Norberg, F. Krok, A. Kozanecka-Szmigiel, M. Saiful Islam, Stephen J. Stokes, A combined total scattering and simulation approach to analyzing defect structure in Bi_3YO_6, Chem. Mater. 22 (2010) 4435–4445. doi:10.1021/cm101130a.

[8] M. Krynski, W. Wrobel, J.R. Dygas, J. Wrobel, M.malys, P. Śpiewak, K.J. Kurzydlowski, F. Krok, I. Abrahams, Ab-initio molecular dynamics simulation of δ-Bi_3YO_6, Solid State Ionics. 245-246 (2013) 43–48. doi:10.1016/j.ssi.2013.05.015.

Specific Metal-Polyoxometallate Interactions in Efficient Electro(Photo)Reduction of Carbon Dioxide

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Of particular interest to the preparation of advanced catalytic materials is efficient utilization of carbon nanostructures and noble metal nanoparticles, their stabilization and intentional activation, as well as organization into two-dimensional arrays, ultra-thin films or three-dimensional networks (e.g. through sequential attraction) on electrode surfaces. They can form nanosized materials with well-defined composition, structure and thickness that exhibit desirable electrocatalytic properties (e.g. toward reduction of CO_2). We explore here the ability of polynuclear inorganic systems to stabilize and derivatize metal and carbon nanostructures. Here certain polyoxometallates of molybdenum or tungsten have been demonstrated to influence supported metal centers in ways other than simple dispersion over electrode area. Evidence is presented that the support can modify activity (presumably electronic nature) of catalytic metal nanoparticles thus affecting their chemisorptive and catalytic properties. Metal oxide nanospecies can generate –OH groups at low potentials that induce proton mobility at the photo(electro)chemical interface.

Our research interests concern development of systems for the reduction (conventional/electrocatalytic or photoelectrochemical) of carbon dioxide. For example, nanosized Ag and Au naoparticles immobilized within ultra-thin films of polyoxometallates and their salts have been considered. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO_2-reduction current densities.

When it comes to photoelectrochemical reduction, we are also going to demonstrate utility of gold and silver nanoparticles (modified or stabilized with Keggin-type polyoxometallates, $PMo_{12}O_{40}^{3-}$, as capping agents; directly or through ligand-exchange) to enhance photocurrents generated by copper(I) oxide photocathodes irradiated with visible light in aqueous solutions. The possibility of generation of localized surface plasmons, will also be considered. Special attention will be paid to stability and controlled reactivity of the proposed systems.

Investigation of WO_3/TiO_2 electrodes for remediation of ciprofloxacin aqueous solutions

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Semiconductor oxides, like TiO_2 and WO_3, have been used for removal of persistent pollutants and contaminants of emerging concern from aqueous environment by heterogeneous photocatalysis (HP). The photocatalyst can also be immobilized on an electrode and then, at a configuration for electrochemically assisted photocatalysis (EHP), the recombination of photogenerated electron/hole pairs is minimized and a higher overall efficiency for photocatalytic activity is achieved. [1].

This contribution reports on the remediation of ciprofloxacin aqueous solutions using WO_3/TiO_2 electrodes irradiated by a solar simulator films. First, a porous WO_3 film was deposited on stainless steel (SS) from an aqueous solution containing Na_2WO_4, H_2O_2, HNO_3 (pH 1.4) under potentiostatic control at -0.35 V (vs. Ag/AgCl) during 20 min, followed by a thermal treatment (450 °C for 30 min). After that, a film of TiO_2 particles was deposited on the surface of the calcined SS-WO_3 electrode from an aqueous suspension of TiO_2 HPW® containing polyethylene glycol, followed by thermal treatment..

SEM images of the surface of SS-WO_3 electrode (Fig. 1a) revealed a homogeneous film with the "cracked mud" structure, with 10 to 35 µm islands. Considering the images taken for the SS-WO_3/TiO_2 electrode (Fig. 1b), it can be concluded that the TiO_2 particles were mainly deposited inside these fissures, resulting in a homogeneous surface. The electrochemical properties of the electrodes were investigated using a solar simulator in aqueous solutions containing 0.1 mol L^{-1} Na_2SO_4 (supporting electrolyte) and 0.1 mol L^{-1} HCOONa (hole scavenger); Ag/AgCl was used as reference, and a Pt wire as counter-electrode (CE). Considering the measurements taken under irradiation and at ambient illumination conditions ("dark"), the SS-WO_3 and SS-WO_3/TiO_2 electrodes exhibited photopotential values of -0.09 V and -0.16V respectively, while the photocurrent corresponded to 15 uA cm^{-2} and 50 uA cm^{-2}, respectively. The highest photocurrent exhibited by the SS-WO_3/TiO_2, in comparison to the SS-WO_3 electrode, can also be observed from the curves of linear voltammetry taken under intermittent irradiation, at Fig 1 (c). These electrodes, irradiated by a solar simulator and polarized at 0.7 V in EHP configuration, were used for remediation of an aqueous solution containing 0.17 mmol $L^{-1}$of the antibiotic ciprofloxacin. For comparison, the studies were also performed in similar conditions without the photocatalyst (remediation by photolysis). After 3 h, ultra performance liquid chromatography with detector fluorescence (UPLC-FLR) analysis revealed a removal of 33% of the antibiotic by photolysis while the SS-WO_3/TiO_2 in EHP configuration exhibited a better performance, with removal of 60% of the ciprofloxacin, (Fig 1 d). Acknowledgment: Fapesp, CNPq, Capes, INOMAT.

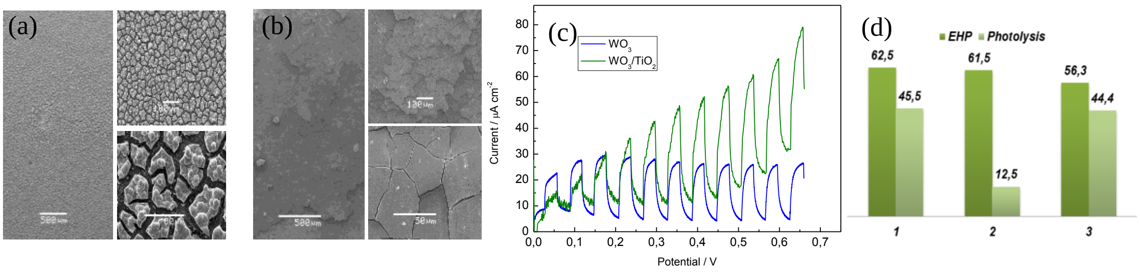

Figure 1. WO_3 and WO_3/TiO_2 electrodes: SEM images WO_3 (a) and WO_3/TiO_2 (b) films deposited on stainless steel; linear sweep voltammetry in aqueous Na_2SO_4 containing HCOONa under intermittent irradiation (c); ciprofloxacin removal after 3h under irradiation with a solar simulator (d).

[1] H.G. Oliveira, L.H. Ferreira, R. Bertazolli, C. Longo, Remediation of 17-α-ethinylestradiol aqueous solution by photocatalysis and electrochemically-assisted photocatalysis using TiO_2 and TiO_2/WO_3 electrodes irradiated by a solar simulator. Water Research, 72, 305-314 (2015).

The impact of non-metal atoms doping in titania onto the photoactivity of the TiO_2NT/pEDOT:Fehcf heterojunction

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Highly ordered titania nanotubes (TiO_2NT) are currently regarded as a promising material for sensors, electrochromic devices, solar cells and supercapacitors, owing to their relatively simple and highly-controlled anodization procedure. However, the usage of titania nanotubes (NTs) as a photoelectrode material is limited to the UV illumination as a result of the wide band gap energy. Thus, many efforts are undertaken to shift its activity towards the visible wave range, e.g. metal or non-metal doping, integration with other metal oxides or deposition of conducting polymer (CP). In some cases also few strategies were implemented simultaneously, i.e. decoration with CdS nanoparticles and further polymer deposition [1]. Obtained results indicates that appropriate optimization of different approaches used in parallel lead to significant improvement of the material activity exhibited under light irradiation comparing to the only one way of material modification.

Here, the study shows the preparation of inorganic–organic heterojunction where ordered, hydrogenated titania nanotubes were infiltrated by nanostructure combining poly(3,4-ethylenedioxythiophene) (PEDOT) with embedded iron hexacyanoferrate (Fehcf, Prussian blue) exhibiting redox activity [2]. The inorganic part (TNT) of heterojunction will be modified by non-metal atoms doping, namely by nitrogen [3], iodine [4] and boron [5] in order to modulate the elemental composition, absorbance ability, electrochemical properties of H-TiO_2NT and finally the energy band alignment of the titania and the polymer part of the composite. The doping is realized according to the elaborated procedure based on the electrochemical process carried out in two-electrode arrangement in the aqueous solution containing the source of particular non-metal atoms, i.e. diethylenetriamine, boric acid and potassium iodide. It should be highlighted that proposed method ensures permanent introduction of non-metal atoms into the titania structure whereas the tubular morphology is preserved and allows direct comparison to the undoped material. The photoactivity will be verified during chronoamperometry measurements performed at the constant potential under prolonged chopped UV-vis radiation while the sample is immersed in the neutral solution of K_2SO_4. Obtained results allows to indicate the type of dopant suitable for achievement of the highest photocurrent and shows promising way to enhance photoactivity of the ordered inorganic/organic heterojunctions.

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[1] G.F. Samu, C. Visy, K. Rajeshwar, S. Sarker, V.R. Subraminian, C. Janaky, Electrochim. Acta 151 (2015) 467.
[2] K. Siuzdak, M. Szkoda, J. Karczewski, J. Ryl, A. Lisowska-Oleksiak, Electrochim Acta 2016, doi: 10.1016/j.electacta.2016.11.102
[3] K. Siuzdak, M. Szkoda, M. Sawczak, A. Lisowska-Oleksiak, New J. Chem. 39 (2015) 2741.
[4] K. Siuzdak, M. Szkoda, M. Sawczak, A. Lisowska-Oleksiak, J. Karczewski, J. Ryl, RSC Adv 5 (2015) 50379.
[5] M. Szkoda, K. Siuzdak, A. Lisowska-Oleksiak, J. Karczewski, J. Ryl, Electrochem Comm 60 (2015) 212.

Study of the Photochromic Properties of Maze-Like MoO_3 Microstructures Prepared by Anodization of Mo Plate

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Photochromism and electrochromism phenomena of transition metal oxides have received considerable attention because of potential applications in *e.g.* display devices [1]. Some metal oxides can be deeply colored by exposing material for irradiation characterized by the appropriate energy (photochromism) or by applying potential (electrochromism) [2]. Among the transition metal oxides, molybdenum trioxide seems to be an ideal example of material which exhibits photochromic properties while intercalation of cations into the MoO_3 structure occurs [3, 4]. The ionic radius of Mo on different oxidation states changes slightly, thus photointercalaction process may occur reversibly [5]. The molybdenum oxide film offers potential application in optical storage systems, display devices and smart windows [6]. The photointercalaction effect observed for MoO_3 layers in contact with Na_2SO_4 aqueous electrolyte has been utilized in an energy storage device.

In this study, MoO_3 films were prepared *via* anodization of molybdenum foil in F ions containing electrolyte. Samples were exposed for UV-vis illumination in aqueous electrolytes provoding different cations. The effect of photointercalated alkali metal cations (Li^+, Na^+, K^+, Cs^+) for optical and structural properties will be shown. Therefore, different techniques: UV-Vis reflectance spectroscopy, Raman spectroscopy and XRD were applied to investigate the impact of intercalation. It will be shown that maze-like morphology of as-prepared MoO_3 films changed due to the long-term illumination as inspected by scanning electron microscopy. Additionally, theenergy band gap narrowing caused by the photochromic effect may affect the photocatalytic properties of intercalated materials.

Financial support from the National Science Center (2012/07/D/ST5/02269) is gratefully acknowledged.

References

[1] Colton, R. J, Guzman, A. M, Rabalais, J. W., Acc. Chem. Res. 11 (1978) 170.
[2] Colton, R. J, Guzman, A. M, Rabalais, J. W., J. Appl. Phys. 49 (1978) , 409.
[3] Shen Y, et al. Mater. Sci. Semicond. Process. 29 (2015) 250.
[4] He T, Yao J., J. Photochem. Photobiol. C 4 (2003) 125.
[5] Pistoia G., International Chemistry Library, Elsevier 1994, Vol. 5.
[6] Pathan H, Min S, Jung K, et al. Electrochem. Commun. 8 (2006) 273.

Hematite/Graphene Bi-layered Photoelectrodes for Efficient Solar Fuel Conversion

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Photoelectrochemical (PEC) water splitting is a promising route for the conversion of solar energy into energy rich hydrogen fuel using water as a reactant. Synthesis of highly efficient semiconductor photoelectrode is the key challenge in this field. The photoelectrode should absorb a major part of visible light from the sunlight, the valence band and conducting band edge of semiconductor should be straddled with the oxygen evolution and hydrogen evolution potential, good stability in electrolyte medium and efficient charge transport properties in the semiconductor. So far, no single electrode satisfies all such criteria. In the quest of suitable semiconductor photoelectrodes, hematite (α-Fe_2O_3) is the earth abundant material, which has an optimum band gap of around 2.1 eV, high theoretical solar-to-hydrogen (STH) efficiency of 16.8%, a suitable band edge position for water splitting reaction and the good stability in broad pH electrolyte medium. However, the hematite suffers from the short hole-diffusion length, poor electronic conductivity, high electron-hole recombination rate, slow charge-transfer kinetics and sluggish oxygen evolution reaction (OER) kinetics still limits its practical STH efficiency. To mitigate these issues, we have developed hematite/graphene bi-layered photoelectrode for the enhanced charge separation and reduced recombination of electron-holes. The direct growth of hematite is achieved by the facile hydrothermal synthesis route via formation of FeO(OH) thin film followed by high temperature calcination in air atmosphere. The thickness of the hematite was controlled by varying the hydrothermal reaction time. The strategic role of graphene is studied by the formation of hematite/graphene bi-layered photoelectrode and the corresponding PEC properties of bi-layer electrode is compared to the pristine hematite photoelectrode. The physico-chemical properties of as synthesized photoelectrodes are characterized using XPS, XRD, Raman Spectroscopy, SEM and TEM. The photoelectrochemical properties are measured using linear sweep voltammetry, chronoamperometry and impedance spectroscopy under 1-sun illumination using three-electrode setup with platinum wire as a counter electrode and RHE as a reference electrode in 1 M KOH electrolyte. For comparison purpose, the dark current is also measured using the same experimental setup in the absence of light.

Fabrication and Characterization of Porous Anodic Titanium Oxide by Pulse Anodization

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Nanotechnology is one of today's most challenging, exciting, and multidisciplinary branches of science. There are a number of subfields of nanoscience, and one of them concerns fabrication of nanomaterials with specific properties. One of the most obvious advantages, provided by nanomaterials, is their greatly developed surface area and high surface to volume ratio. The synthesis of new functional materials has also embraced $TiO_{2,}$ especially with well-ordered nanoporous/nanotubular architectures.

To the date, titanium dioxide nanostructures have been synthesized by various methods including, sol–gel, hydrothermal/solvothermal processes, electrospinning, electrospray, electrodeposition and electrochemical anodization techniques [1]. The latter one, has been classified as one of the most attractive synthetic route for the fabrication of highly ordered nanoporous and nanotubular metal oxides. The attractiveness of this preparation strategy results from its simplicity, low costs and the ability to control of the surface morphological parameters of anodic titanium dioxide (ATO) films. Unlike a constant DC potential was most often used in literature report for generation of TiO_2 nanopores/nanotubes with straight and smooth nanochanell, a use of altering the applied potential is the easiest way to modify the nanoscale architecture of highly-ordered smooth-walled TiO_2 layers and produce three-dimensional nanotube/nanopore arrays with bamboo-type morphology [2], branched [3] and multiple-layer structures [4]. The development of novel, more efficient TiO_2 layers with higher surface area and tailorable dimensions is extremely worthy to study in various applications, especially in the area of energy conversion and storage.

In the light of above mentioned issues, we present in this work the fabrication of TiO_2 nanopore arrays by pulse anodization (PA) of the titanium foil under specific alternating-voltage conditions in an ethylene glycol solution containing NH_4F (0.38 wt%) and H_2O (1.79 wt%). The morphology, structure and photoelectrochemical properties of the generated nanoporous TiO_2 layers were characterized in detail.

Acknowledgments:
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References:

[1] M. Ye, D. Vennerberg, C. Lin, Z. Lin, J. Nanosci. Lett., 2 (2012) 1-17
[2] S. P. Albu, D. Kim, P.Schmuki, Angew. Chem., 47 (2008) 1916 –1919
[3] G. Butail, P.G. Ganesan, R. Teki, R. Mahima, N. Ravishankar, D.J. Duquette, G. Ramanath, Thin Solid Films, 519 (2011) 235-238
[4] D. Guan, Y. Wang, Nanoscale, 4 (2012) 2968–297

Fabrication of 3D Nanoporous Anodic Titania as a Promising Photoelectrode Material

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Nowadays, nanotechnology is interdisciplinary branch of sciences, which develops rapidly and intensively. After anodic aluminum oxide (AAO), the next nanoporous material which have attracted tremendous interest of researchers around the world, is nanoporous anodic titanium oxide (ATO) formed by anodization. We have witnessed a significant advancement in titanium dioxide materials research over the past decade. Ordered porous ATO has gained a lot of attention due to a successful combination of functional chemical and physical properties with a well controllable nanoarchitecture, which make its one of the most important material, suitable for a variety of technological applications including photocatalysis, photovoltaics, sensors and templates for deposition of secondary nanomaterials [1-2].

Taking into the above mentioned importance of this nanostructured material, the main objective of this work is to investigate the growth of anodic titanium dioxide structures, particularly in the form of TiO_2 nanopore arrays, by a self-organized anodization of the Ti mesh in a viscous electrolyte based on ethylene glycol containing fluoride ions. It is well known that the modification of anodization conditions affects the morphology of formed TiO_2 nanopore array. In this context, we examine the anodizing potential and process duration as main parameters that influence the morphology and structure of ATO layers. Moreover, photoelectrochemical properties of as-prepared nanoporous TiO_2 photoelectrodes are explored.

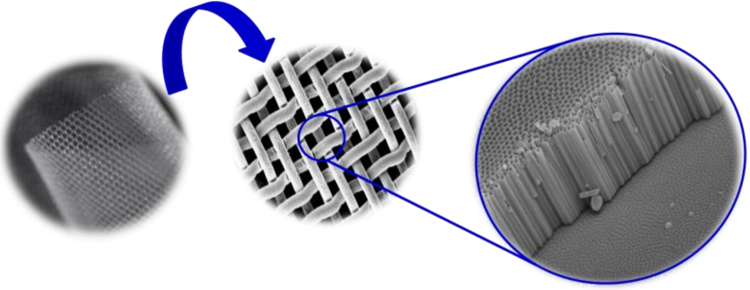

Fig. 1 Schematic representations of the 3D TiO_2 nanopores formed on Ti mesh.

Acknowledgments:

This research was partially supported by the National Science Centre, Poland (Decision No. DEC-2013/09/N/ST5/02487).

References:

[1] A. Ghicov, P. Schmuki, Chem. Commun., (2009) 2791-2808
[2] P. Roy, S. Berger, P. Schmuki, Angew. Chem. Int. Ed., 50 (2011) 2904-2939

Photoelectrochemical Properties of Nanoporous Anodic Tin-Oxide Layers

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Recently, nanostructured SnO_2 materials are extensively investigated due to their promising properties and many potential applications including photovoltaics, solid-state gas sensors, catalysts, etc. Within this context, a simple anodic oxidation (anodization), widely known as an effective, cheap and versatile method for the synthesis of nanoporous or nanotubular oxide layers on the surface or various metals [1], seems to be a very promising strategy also for fabrication SnO_2-based photoanodes [2–4]. The main problem which limits potential applications of such kind of anodic tin oxide films is their relatively poor mechanical stability being a result of the presence of cracks in the internal structure [2]. However, very recently we proposed a new approach to obtain crack-free porous anodic tin oxide layers based on anodic oxidation of Sn in alkaline electrolyte at low applied voltages [3]. Furthermore, the most important drawback of SnO_2 is that it has relatively high band gap (> 3 eV). As a result, only the UV light can be absorbed by this semiconductor. Therefore, the main challenge in improving energy conversion efficiency of photoanode is to reduce band gap of semiconductor in order to increase the absorption in the visible range. As it was recently proved, an oxide layer grown on Sn substrate during anodization consists of an amorphous, non-stoichiometric SnO_x with a quite large content of Sn^{2+} defects and oxygen vacancies which are responsible for a relatively high absorption in the visible range [4].

Therefore, here, we present some recent results on anodic formation of crack–free nanoporous tin oxide layers by simple one-step anodic oxidation of low purity Sn foil in alkaline electrolytes at various anodizing conditions such as applied potential and electrolyte concentration.

The morphology and composition of as synthesized nanostructured photoanodes were investigated by various techniques (e.g. SEM, XRD, XPS) and correlated with the conditions applied during fabrication process. Finally, optical band gap energies were determined and photoelectrochemical characterization of samples was carried out using a photoelectric spectrometer. It was proved that photoelectrochemical activity of anodic film can be modified by tuning the concentration of Sn^{2+} defects and the crystallinity of the sample via simple thermal annealing under controlled conditions.

Acknowledgement
This work was partially supported by National Science Centre, Poland (Project no. 2014/13/D/ST5/02750).

Literature references

[1] K. Lee, A. Mazare, P. Schmuki, Chem. Rev. 114 (2014) 9385–9454.
[2] L. Zaraska, K. Syrek, K.E. Hnida, M. Bobruk, A. Krzysik, T. Łojewski, M. Jaskuła, G.D. Sulka, Electrochim. Acta 205 (2016) 273–280.
[3] L. Zaraska, D. Gilek, K. Gawlak, M. Jaskuła, G.D. Sulka, Appl. Surf. Sci. 390 (2016) 31–37.
[4] A. Palacios-Padros, M. Altomare, K. Lee, I. Diez-Perez, F. Sanz, P. Schmuki, Chem. Electro. Chem. 1 (2014) 1133–1137.

Supercapacitors based on nanoporous carbons derived from MOF-525

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Nanoporous carbons (NPCs) have attracted wide attention in the research community for electrochemical capacitors because of their excellent chemical and mechanical stabilities, good electrical conductivity, and high surface area. In this study, we report NPCs prepared by direct carbonization of a Zr-based porphyrin MOF (MOF-525). The Zr-based porphyrinic MOF, MOF-525, whose structure is built up from the $Zr_6O_4(OH)_4$ oxoclusters bounded to tetracarboxyphenylporphyrin (H_4TCPP) ligands. The introduction of metals (e.g., Co, Fe, Ni and Zr) in carbon matrix promotes the electrochemical properties due to their effect of catalytic graphitization of amorphous carbon. Because the metallic species integrated with the whole structure, it is important to remove the metallic species for the purpose of obtaining high surface area carbons. These metallic MOFs generated extremely porous carbon products after a post-acid wash treatment. In this work, MOF-525 is directly carbonized at 800 °C under N_2 flow in a one-step approach without addition of any carbon source. We synthesized five different average particle sizes of MOF-525 from 100 to 800 nm utilizing singular precursors without any additional carbon resources. The precursor amount of MOF-525 during the process was changed to 0.9 g, 1.1 g, 1.35 g, 2.0 g, and 2.7 g; thus the obtained MOF-derived carbon (MDC) samples were designated as MDC0.9, MDC1.1, MDC1.35, MDC2.0, and MDC2.7, respectively. The obtained MDCs show superior electrochemical performance as supercapacitors. Also, the size effect on electrochemical properties of MDCs is investigated and discussed.

Table 1 Surface areas and total pore volumes of MDC0.9, MDC1.1, MDC1.35, MDC2.0, and MDC2.7. [a] BET method, [b] t-plot method, [c] NLDFT method.

Sample	S_{BET}[a] (m^2 g^{-1})	S_{micro}[b] (m^2 g^{-1})	S_{micro}/S_{BET} (%)	V_{pore}[c] (cm^3 g^{-1})	V_{micro}[c] (cm^3 g^{-1})	V_{micro}/V_{pore} (%)	Specific capacitance (F/g)
MDC0.9	603	550	91.2	0.93	0.18	19.0	296
MDC1.1	773	567	73.4	0.96	0.21	21.9	438
MDC1.35	786	688	87.5	0.92	0.23	25.0	426
MDC2.0	534	453	84.8	0.73	0.14	19.2	210
MDC2.7	393	329	83.7	0.40	0.11	27	186

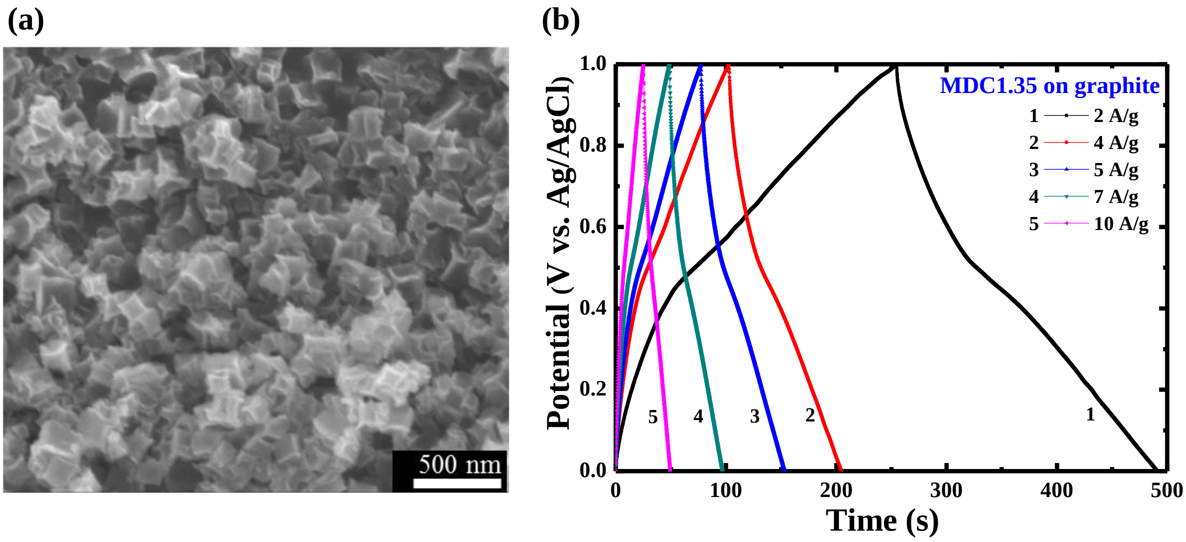

Fig. 1 (a) SEM images of M1.35 nanoparticles (b) charge−discharge curves of MDC1.35 electrode measured at different current densities.

Photoactivity of Copper Selenide Thin Films Electrodeposited from a Choline Chloride-Urea Electrolyte

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In the emerging field of thin-film photovoltaics, electrodeposition appears as a promising technology to decrease the fabrication costs, inherently high in vacuum-based methods, while being also more efficient in terms of reactant and energy consumption. Inorganic compound semiconductors composed of transition metals and chalcogen elements (Te, Se, S) exhibit some of the most suitable properties, in particular with respect to their bandgap energy, for their implementation as absorber layers in solar cells. Although $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) have shown very high conversion efficiency in laboratory and modules, the limited availability of some of their constituents has led scientists to consider alternative materials such as CZTSe (Copper-Zinc-Tin-Selenide), made of earth-abundant elements and, therefore, more sustainable.

Previously, we have conducted the electrodeposition of selenium in the 1:2 choline chloride – urea deep eutectic electrolyte at high temperatures (110°C) to promote the formation of the conductive "grey selenium" allotrope rather than the non-conductive "red selenium". Through voltammetric and potentiostatic experiments, the following electrochemical processes were evidenced [1]:

$$\mathrm{Se(IV)} + 4\,e^- \rightleftarrows \mathrm{Se(0)}$$
$$\mathrm{Se(0)} + 2\,e^- \rightleftarrows \mathrm{Se(-II)}$$

In the presence of metal precursors, the second reaction (dissolution) proceeds at less negative potentials, being coupled with the formation of a metal selenide deposit and binary metal-selenium compounds can thus be electrodeposited in one step by a proper choice of the deposition potential [2].

In the present work, we investigate the electrodeposition of copper-selenium binary compounds from a SeO_2/Cu_2O mixture in choline chloride-urea at 110°C. The copper-selenium binary compounds are characterized by XPS, EDX and XRD.

Photo-electrochemical measurements are conducted to characterize the semiconductor behavior and its photochemical stability. Current-potential curves in the dark and under illumination as well as current-potential plots obtained with chopped light are recorded at room temperature in the presence of 0.01 M Na_2SO_4. Further characterization is obtained by a photoconductivity study conducted in an I_3^-/I^- electrolytic solution.

[1] Bougouma, M., Van Elewyck, A., Steichen, M., Buess-Herman, C., Doneux, T. (2013). Selenium electrochemistry in choline chloride-urea deep eutectic electrolyte. *Journal of Solid State Electrochemistry*, *17*(2), 527–536.
[2] Bougouma, M., Doneux, T., Legma J.B., Buess-Herman, C (2014). Etude électrochimique du système Zn-Se en milieu eutectique chlorure de choline-urée. J. Soc. Ouest-Afr. Chim. 038, 1 – 14.

Electronic and optical properties of B/P co-doped g-C_3N_4 monolayer nanosheets

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In recent years, a large-scale transition toward non-polluting, abundant, inexpensive, and renewable energy sources, particularly sunlight energy, is expected to occur owing to the significant population increase, rapid growth of energy consumption, and reduction in oil and gas supplies. Photoelectrochemical (PEC) water splitting with semiconductor photoelectrode has attracted much interest. Selecting an appropriate semiconductor is a key factor to achieve high PEC performance (*1*). Among various semiconductors used in PEC application, a polymeric semiconductor based on graphitic carbon nitride (g-C_3N_4 or GCN) has attracted tremendous attention owing to its undeniable properties including thermal and chemical stabilities. However, its photocatalytic activity still needs to be improved because of its low surface area, high recombination rate of photogenerated carriers, and poor optical absorption above 420 nm. Therefore, several strategies, such as elemental doping and employing different materials to construct GCN-based heterojunction have been proposed so as to enhance its photoconversion efficiency (*2*).

Herein, we studied the effect of B/P-codoping on electronic and optical properties of GCN monolayer using density functional theory (DFT) simulations. The calculated energy band structure indicated that the incorporation of B and P into a hexagonal lattice of GCN monolayer with triazine-based structure reduced the energy band gap from 3.1 for pristine GCN nanosheet to 1.9 eV for the co-doped system, which extended light absorption towards visible region. Moreover, according to our data analysis of optical absorption spectra and dielectric function (imaginary part), the co-doped system exhibited an improved absorption intensity in the visible region and more electronic transitions (n-π^*), which is prohibited in the pristine GCN (Figure 1a). These transitions could be attributed to charge redistribution upon doping, caused by distorted configurable B/P-codped GCN (Figure 1b)(*3*). It should be noted that this result was also confirmed by both electron density and Mulliken charge population calculations. Therefore, B/P-co-doped GCN is expected to be a promising photoelectrode candidate in PEC water splitting reactions leading to efficient solar H_2 production.

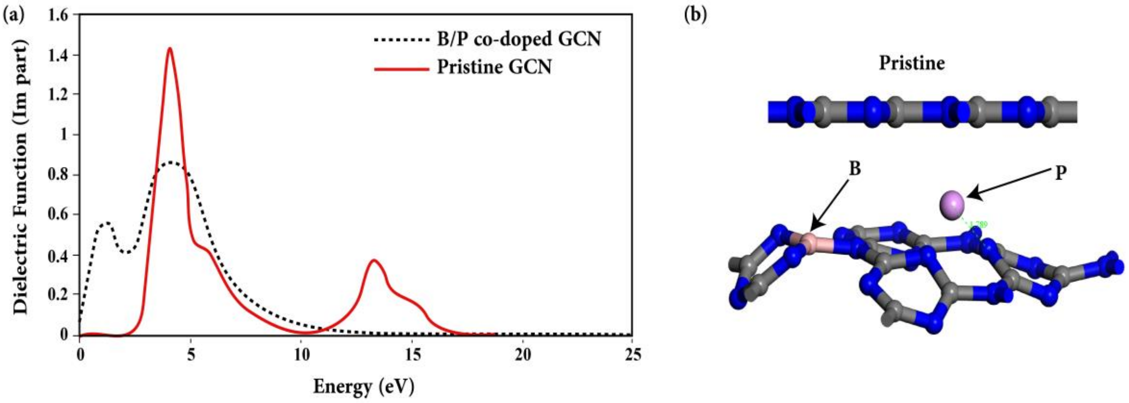

Figure 1. (a) Dielectric function (imaginary part), and (b) the side view of pristine and B/P co-doped GCN. Gray and blue represent C and N atoms, respectively.

1. M. Grätzel, Photoelectrochemical cells. *Nature* **144**, 338-344 (2001).
2. W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chemical Reviews* **116,** 7159-7329 (2016).
3. Y. Chen, B. Wang, S. Lin, Y. Zhang, X. Wang, *The Journal of Physical Chemistry C* **118**, 29981-29989 (2014).

Dual Modification of Hematite Photoanode by Sn-doping and Nb_2O_5 Layer for Water Oxidation

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Porous hematite (α-Fe_2O_3) films doped with Sn(IV) and coated with an ultrathin (∼2 nm thick) Nb_2O_5 passivation layer were synthesized, and the photoelectrochemical (PEC) water oxidation performance and durability of the hematite were examined in detail. As compared to hematite samples modified by either doping or passivation, dual-modified hematite exhibited a promising PEC water oxidation performance under AM 1.5 irradiation. A stable photocurrent was maintained under prolonged irradiation over 24 h, while O_2 was produced from water with a Faradaic efficiency of over 80% without showing any sign of deactivation. This performance and durability could be decoupled into separate effects of Sn doping and Nb_2O_5 layer via in-depth surface characterization and electrochemical analyses. Sn doping increased the donor density (N_d) of bare hematite by a factor of 20 and significantly improved its conductivity, leading to enhanced charge transfer efficiency. The Nb_2O_5 layer exerted an effect similar to Sn doping because of the diffusion of a fraction of Nb(V) into the hematite lattice during the annealing process at 700 °C. The primary effect of the Nb_2O_5 layer is to passivate the hematite surface and make the surface more reactive toward the oxygen evolution through water oxidation. These effects are synergistically combined in the dual-modified hematite electrode [1].

Reference

[1] T.W. Jeon, A.D. Bokare, D. S. Han, A. Abdel-Wahab, H. Park, W. Choi, Appl. Catal. B: Environ. 201 (2017), 591-599.

The Effects of Blended Cathode Materials for All-solid-state Li-ion Batteries

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Currently, rechargeable lithium-ion batteries (LiBs) are widely used for xEVs such as hybrid, plug –in hybrid and electric vehicles as a power source. However, the safety concern of the LiBs is still one of the major challenges due to using flammable organic liquid electrolytes. All-solid-state batteries (ASSB) may be promising candidate to solve the problem because it uses non-flammable inorganic solid electrolytes as an electrolyte and separator[1-2].

The effects on the blended cathode materials for all solid state lithium-ion batteries with an oxide based solid electrolyte were studied[3]. The parent materials can minimize their shortcomings by blending two cathode materials and the blending ratios may be tailored for high energy, power density with improved stability. In this report, we investigated the influence of blended cathode materials such as $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2/LiMn_2O_4$ and $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2/LiFePO_4$ on the structure, cycling stability, rate performance and thermal stability by tools such as Powder X-ray Diffraction, Field-emission SEM, Inductively coupled plasma atomic emission spectrometer (ICP-AES), high resolution transmission electron microscopy (HR-TEM), and a Differential Scanning Calorimeter (DSC).

References

1. N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Saski, Enhancement of the High-Rate Capability of Solid-State Lithium Batteries by Nanoscale Interfacial Modification, Adv. Mater (2006), 18, 2226-2229
2. .J. H. Choi, C. H. Lee, J. H. Yu, C. H. Doh, S. M. Lee, Enhancement of ionic conductivity of composite membranes for all-solid-state lithium rechargeable batteries incorporating tetragonal $Li_7La_3Zr_2O_{12}$ into a polyethylene oxide matrix, J. Power Sources 274 (2015) 458-463
3. S. B. Chikkannanavar, D. M. Bernardi, L. Liu, A review of blended cathode materials for use in Li-ion batteries, J. Power Sources 248 (2014) 91-100

Light Driven Water Splitting with Cyanide-based Coordination Compounds Incorporating [Ru(bpy)$_3$] Fragments

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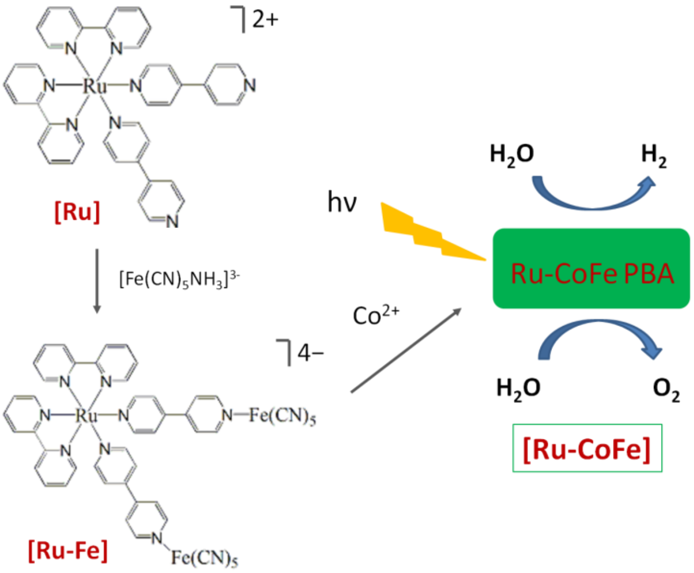
Prussian Blue analogues have recently been investigated as photoactivated water oxidation catalysts in the presence of a [Ru(bpy)$_3$]$^{2+}$/persulfate system.[1] Although cobalt hexacyanometalates exhibit catalytic activity with a high quantum yield (≤88%), the system is deactivated during catalysis due to the decomposition of [Ru(bpy)$_3$]$^{2+}$ complex. Herein, a synthetic approach was introduced to prepare a cyanide-based coordination compound that mimics molecular dyads. The system involves two significant structural units; a) ruthenium ions surrounded with pyridyl groups operating as chromophores and cobalt ions surrounded with nitrogen atoms that serve as water oxidation & reduction catalysts. Furthermore, the performance of these systems for light-driven water oxidation and reduction processes will be presented.

1. Goberna-Ferrón, S.; Hernández, W. Y.; Rodríguez-García, B.; Galán-Mascarós, J. R. *ACS Catal.* **2014**, *4*, 1637-1641.



Electrochemical synthesis of silver nanoparticles and their influence on Raman spectra of polypyrrole

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A new synthetic procedure of electrochemical-chemical preparation of nanocomposites of polypyrrole-silver halides [1] permits extended studies on the mechanism of formation and stability of Ag nanoparticles in the polymer matrix. The electrochemically controlled step-wise reduction of the pristine AgCl-polypyrrole composite reveals conditions for formation of Ag nanoparticles active in the enhancement of Raman spectra of polypyrrole (Fig.1).

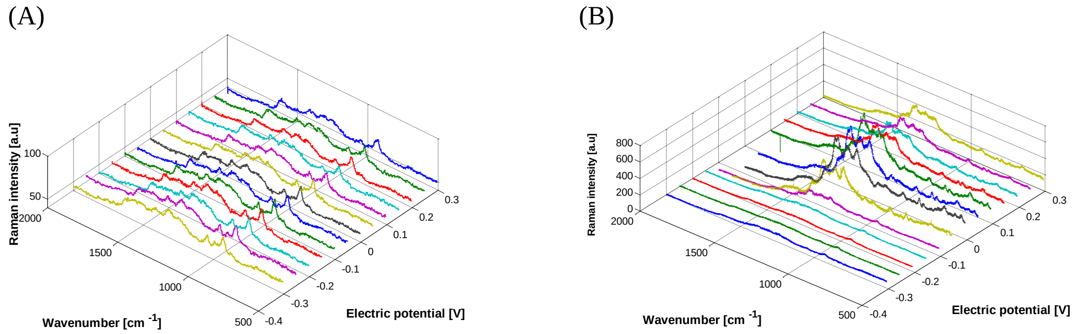

Fig.1 Raman spectra, at 647 nm laser excitation, recorded during a step-wise change of the electrode potential in 0.1 M KCl: (A) polypyrrole and (B) polypyrrole-AgCl (unpublished own research).

The intensity enhancement of the polypyrrole Raman bands, appearing in the spectra (B) of the composite, can be considered as the effect due to the silver nanoparticles, known well in the surface enhanced Raman spectroscopy (SERS).

The characteristic Raman bands of polypyrrole of the pure polymer [2,3] and the studied nanocomposite shall be assigned. The spectroelectrochemical data will be subjected to the statistical chemometric analysis [4] and thoroughly compared. A corresponding specific changes in cyclic voltammograms of the composite due to its redox processing, that results in the SERS activity of the silver particles, will be discussed. The surface morphology of the composite at the selected stages of the redox processing, monitored *ex-situ* by using scanning electron microscopy (SEM), will be under focus as well.

[1] K. Wójcik et al., J. Solid State Electrochem., (2016), doi: 10.1007/s10008-016-3429-7
[2] A. Kępas et al., Polish J. Chem., (2007), 81, 2207
[3] M. Grzeszczuk et al., Synthetic Metals, (2010), 160, 636
[4] M. Grzeszczuk, A. Grańska, R. Szostak, Int. J. Electrochem. Sci., (2013), 8, 8951

A new synthesis of polypyrrole with silver nanoparticles and application as SERS platform

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There are many methods of the nanocomposite syntheses, described in the literature, where a conductive polymer coats or surrounds silver nanoparticles. However, only a few works describe compact polymer matrices, because of the chemical preparation of the polymer, which makes it necessary to mechanically compress such chemical composites on an electrode. Silver can be introduced into a polymer matrix during polymerization, when silver cation is reduced while the monomer is oxidized [1]. A silver cation may also oxidize the reduced polymer with the simultaneous precipitation of the metal [2]. It is possible to employ electrodeposition of silver from a silver (I) nitrate (V) solution [3]. Finally, at first the polymer can be obtained with the chloride counterion (chemically), and later on the purified polymer can be added to a silver (I) nitrate (V) solution causing the precipitation of silver chloride nanoparticles [4].

A new method of nanocomposites synthesis was developed by our team (Fig.1). The process consist of three stages: electrochemical polymer electrosynthesis, the electrochemically driven ion exchange of the original matrix anion to a halide, and precipitation of silver (I) chloride through the immersion of a dry polymer matrix in silver (I) nitrate (V) solution. As the concentration of silver (I) nitrate (V) decreases, more and more nanoparticles of silver chloride appear on the surface of the polymer matrix, so it is possible to control the distribution of nanoparticles [5]

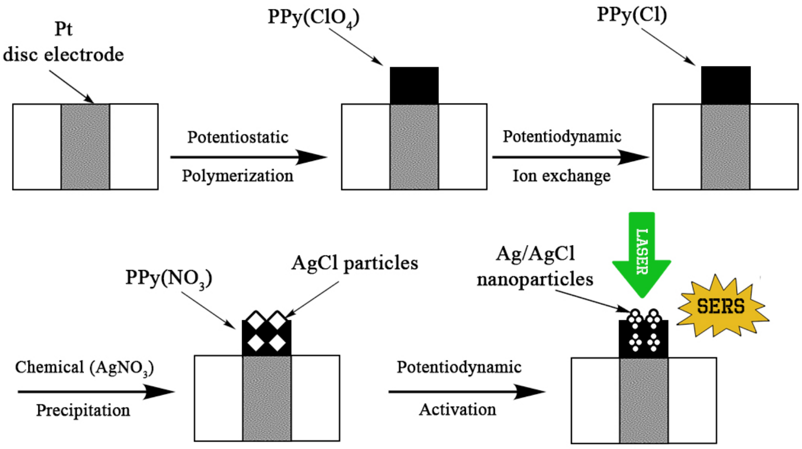

Fig.1 Synthesis of the composite of polypyrrole with silver/silver chloride nanoparticles [5]

This process results in silver chloride nanoparticles obtained in a course of the reduction/oxidation of the composite by means of cyclic voltammetry.

Electrical and electrochemical properties were measured by cyclic voltammetry and electrochemical impedance spectroscopy. Morphology of surfaces was determined using scanning electron microscopy. A significant Raman signal enhancement was obtained on the silver chloride/silver polypyrrole nanocomposite for an analyte in solution, i.e. the surface enhanced Raman spectroscopy (SERS) has evolved.

[1] A. Chen et al., Chem. Commun., (2005), 1863
[2] P. Xu et al., Langmuir, (2010), 26(11), 8882
[3] T. Rapecki et al., Electrochimica Acta, (2013), 106, 264
[4] J. Skodova et al., Polym. Chem., (2013), 4, 3610
[5] K. Wójcik et al., J. Solid State Electrochem., (2016), doi: 10.1007/s10008-016-3429-7

Photocurrent Switching Effect on Nanostructured Layered $Bi_{14}O_9S_{12}$ Electrodes

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A large number of bismuth semiconductor compounds (oxyhalides BiOCl, BiOBr, BiOI; oxysulfides Bi_2O_2S, Bi_2OS_2, $Bi_3O_3S_2$, $Bi_4O_4S_3$, $Bi_{18}O_{15}S_{12}$) have a layered structure. The interest to bismuth oxyhalides is connected mainly to their high photocatalytic activity and a possibility to be applied for solar energy conversion, whereas oxysulfides constitute a recently discovered class of compounds which can exhibit superconductivity [1]. Furthermore, they can demonstrate a high photoelectric activity. A photoelectrochemical behavior of bismuth oxyhalides, vanadate $BiVO_4$, and sulfide Bi_2S_3 has been already thoroughly studied, while photoelectrochemistry of bismuth oxysulfides is currently at an early stage of development. In particular, the photoelectrochemical behavior of Bi_2O_2S films and Bi_2O_2S/In_2O_3 heterostructures has been reported [2].

In this study the photoelectrochemical properties of bismuth oxysulfide films obtained by chemical bath deposition method on conductive FTO substrates was investigated. The deposited bismuth oxysulfide films have a highly-developed microstructure formed by randomly oriented platelets several hundred nanometers long and several tens nanometers thick (Fig. 1a). A crystallite layered structure was confirmed by TEM (Fig. 1b). Due to such structure the deposited films are characterized by a high “surface-to-volume” ratio providing a short path of charge carriers captured by an electrolyte.

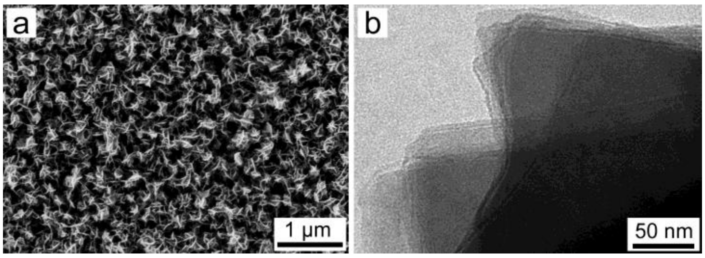

Fig. 1. (a) SEM image of the surface, (b) TEM image for $Bi_{14}O_9S_{12}$ film.

A qualitative and quantitative composition of the bismuth oxysulfide films was determined by XRD, EDX, XPS and chemical analysis. These studies have demonstrated that the crystal structure and formula unit ($Bi_{14}S_{12}O_9$) of the synthesized films differ from oxysulfides that have been described in the literature.

Bi_2S_3 and Bi_2O_2S are known as compounds, which demonstrate *n*-type semiconductor behavior in aqueous electrolyte solutions generating anodic photocurrent due to electrolyte species oxidation (sulfide-anions, water molecules) by photoholes or as a result of a photocorrosion process [2]. The synthesized $Bi_{14}S_{12}O_9$ films also generate an anodic photocurrent in an aqueous Na_2SO_3 solution or in solutions containing other photoholes acceptors (Fe^{2+}, $[Fe(CN)_6]^{4-}$). Anodic photocurrent spectra linearization in $(Yh\nu)^{0.5} - h\nu$ coordinates has proven the presence of indirect optical transitions with a band gap of 1.23 eV. Incident photon-to-current conversion efficiency of anodic photocurrent reaches 60% at λ=400 nm in Na_2SO_3 solution.

A photocurrent switching effect for $Bi_{14}S_{12}O_9$ films in solutions containing photoelectron acceptors ($[Fe(CN)_6]^{3-}$, Fe^{3+}) was discovered. The anodic photocurrent decreases gradually and changes to a cathodic one when a more negative potential is applied. This effect is reversible and reproducible during a repeated cycling of electrode potential. The cathodic photocurrent is observed starting from a certain minimal oxidizer concentration in electrolyte ($c > 10^{-3}$ M) and it significantly exceeds the anodic photocurrent value.

References

[1] X.Zhang, Y.Liu, G.Zhang, Y.Wang, H.Zhang, F.Huang, *ACS Appl.Mater. Interfaces* 7 (2015) 4442.
[2] A.L.Pacquette, H.Hagiwara, T.Ishihara, A.Gewirth, *J.Photochem.Photobiol. A.* 227 (2014) 27.

Characterization of Chalcogenide Semiconductor Quantum Dots by Metal Underpotential Deposition

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Metal chalcogenide semiconductor quantum dots (QDs) are prospective materials for solar cells, thermoelectric applications, photoconductive detectors, photocatalysts, light-emitting devices, field-effect transistors, memory elements, etc. Physical and electrochemical properties of individual QDs are size-dependent and the sizes of QDs are most commonly measured by optical methods, which are not always convenient, especially when opaque electrodes are concerned.

In this work we present the size dependent underpotential deposition (upd) of metal on chalcogenide QD [1] as the electrochemical means of QD size characterization and also the measurement of electroactive surface area of QD-sensitized composite electrodes [2] which proves to be helpful when the upd proceeds selectively on QDs of the QD-sensitized electrodes.

Metal chalcogenide (CdSe, CdS, etc.) QDs were deposited onto conductive substrate and semiconductor oxide (TiO_2, ZnO, etc.) by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR). Despite the CBD and SILAR concede the precise control of the QD size uniformity to QD synthesis with the use of stabilizing shells, these methods provide perfect electric contacts in QD ensembles and heterostructures. The QD size was controlled by variable conditions (temperature, time, concentration of precursors) of the deposition procedure and the temperature in the post-synthesis thermal treatment in Ar medium. The QDs in the QD films and in heterostructures were characterized by cyclic voltammetry and potentiodynamic electrochemical impedance spectroscopy. The use of the two methods helped to distinguish the upd from background processes in complex cases when the upd current was masked by the background current. Analysis of the variable frequency response provided the upd potential measurement from potentiodynamic profiles of charge transfer resistance.

The increase of the substrate particle diameter from few nm to almost bulk dimensions resulted in a positive shift of the upd starting potential by approx. 0.2–0.4 V, and the size effect was dependent on the chalcogenide. The discovered size effect showed some similarity with the size effects reported in literature for metal upd on metal particles. However, the size effects in metal upd on semiconductor chalcogenides were observed at smaller particles than those in metal upd on metal particles.

The selective upd of metal on QDs of QDs/TiO_2 and QDs/ZnO electrodes provides the opportunity to evaluate the electroactive surface area of the QD sensitizer which is the fraction of the total electrode surface area responsible for the QD sensitized anodic photoelectrochemical reactions in quantum dot-sensitized solar cells (QDSSCs). Photoholes generated in QDs are trapped by hole scavengers on the sensitizer surface, while electrons are injected into a wide bandgap semiconductor component of the nanostructured electrode. The measurement of the electroactive surface area of the composite electrodes helps to discover relative roles of the sensitizer photoelectrochemical efficiency and the electrode surface area in the photocurrents of QDSSCs.

References

1. Y.M. Aniskevich, M.V. Malashchonak, P.V. Chulkin, G.A. Ragoisha, E.A. Streltsov. *Electrochim. Acta*. 220 (2016) 493.
2. M.V. Malashchonak, E.A. Streltsov, G.A. Ragoisha, M.B. Dergacheva, K.A. Urazov. *Electrochem. Commun*. 72 (2016) 176.

CVD graphene decorated with colloidal titanium oxide nanocrystals: (photo)electrochemical characterization and electroanalytical applications

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Electroanalytical sensors based on the use of graphene (G) can benefit from its important characteristics: excellent electrical conductivity, high surface area and mechanical strength [1]. The peculiar properties of graphene can be extended by further functionalization with organic and inorganic materials. In this work, we present a solution-based procedure [2] for manufacturing UV-light absorbing and photoactive hybrid materials, based on CVD graphene layers decorated with colloidal titanium oxide nanocrystals (NCs), surface functionalized with 1-pyrene butyric acid.

The physical-chemical properties of the manufactured hybrid materials have been investigated by (photo)electrochemical characterizations. In particular, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy measurements recorded in the presence of an outer- or an inner-sphere probe ($[Ru(NH3)_6]Cl_3$ and $K_4[Fe(CN)_6]$, respectively allowed to study the electron transfer and the electrochemical properties of the electrodes modified with the prepared hybrid materials.

The immobilization of the pyrene-coated TiO_2 NCs on the graphene platform increases its electroactivity, its capacitive behaviour and the photo-electrochemical response, preserving concomitantly its high charge mobility. The results show an enhancement of the photocurrent of 50% with respect to that of bare graphene based electrodes and a long transient decay time ($\tau = 185 \pm 2$ s), studied by the transient photocurrent decay that occurs immediately after UV-light illumination.

The manufactured composite is an interesting optically transparent photoactive material for manufacturing photoanodes to integrate in solar cells or photodetectors and for fabricating components to apply in FETs or (photo)electrochemical sensors. For example, the electroanalytical performances of the devices, tested for the detection of some analytes of medical and pharmaceutical interest (*e.g.* dopamine, norepinephrine), show promising results.

References

[1] K.S. Noselov et al., Nature, 490, (2012), 192-200.
[2] C. Ingrosso et al., ACS Appl. Mater. & Interfaces, 7, (2015), 4151-4159.

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Synthesis of platinum nanoparticles/graphene nanoribbon composites for biosensing application

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We proposed a large-scale synthesis for graphene nanoribbons (GNRs) with little amount of H_2SO_4 usage (0.1 mg/ml of nanotube concentration in acid solution) and achieved nearly 100% yields by unzipping carbon nanotubes. XPS result (Fig. 1(a)) shows that, with the longitudinal unzipping method, abundant oxygen related functional groups (carboxyl group, carbonyl group and hydroxyl group) could be obtained at the edges of GNRs, which gave advantages in further material design. In this work, the functional groups assisted the reduction of platinum precursor to form platinum nanoparticles (PtNPs) and target sensing. Material characterization suggested that PtNPs were successfully modified on the surface of GNRs and played a role as connecting nodes to synergize the synthesized nanoribbons with a size of 3.01 ± 0.68 nm (Fig. 1(b)). GNRs served as conductive substrates and PtNPs provided superior conductivity and lowered the charge transfer resistance (R_{ct}: 410.2 Ω (GNRs) and 135.3 Ω (PtNPs/GNRs), Fig. 1(c)). The PtNPs/GNRs composite material could be used in a non-enzymatic sensor toward both oxidative and reductive analytes. To proof the concept, important biomarkers including hydrogen peroxide (H_2O_2) and β-nicotinamide adenine dinucleotide (NADH) were chosen to demonstrate the feasibility of the designed sensor. PtNPs/GNRs could significantly improve the sensing performance with its great ability in electrochemical catalysis. With amperometric i-t analysis, the sensitivity of PtNPs/GNRs modified electrode toward H_2O_2 and NADH were 378.5 and 724.3 μA mM^{-1} cm^{-2}, respectively. PtNPs decorated GNRs modified electrode proved to be a promising composite material for electrochemical biosensing with great sensitivity, selectivity and stability.

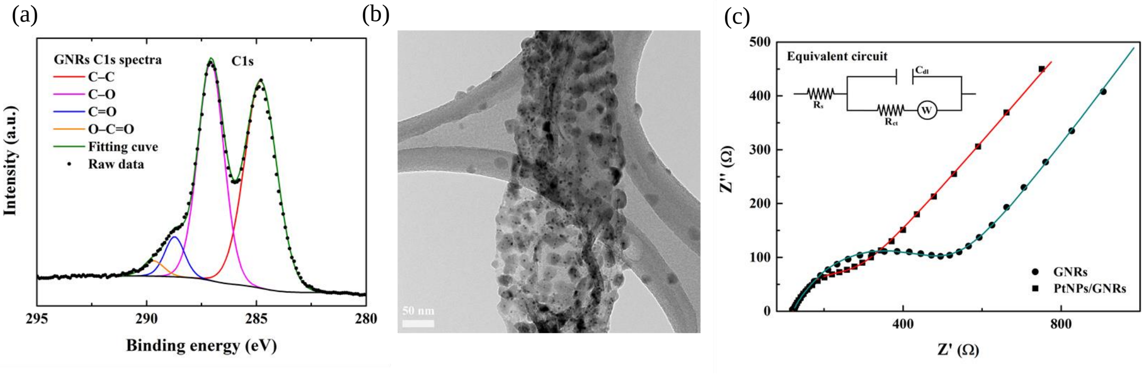

Fig. 1. (a) XPS C1s spectrum of GNRs, (b) TEM image of PtNPs/GNRs, (c) Nyquist plots of GNRs and PtNPs/GNRs.

Metal-organic framework/PEDOT:PSS nanocomposite as high-performance electrode materials for supercapacitors

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Metal–organic frameworks (MOFs), emerging as a novel class of porous crystalline, are constructed with metal-based nodes and organic linkers. This is due to MOFs' outstanding characteristics such as ultrahigh accessible surface areas (highest reported value: ~7000 m^2g^{-1}), tunable pore sizes and ordered crystalline structures. Recently, few pioneering work had demonstrated the potentials of pristine MOFs serving as electrode materials of supercapacitors (SCs), which generate electric double layer capacitance (EDLC) with its high accessible surface areas. However, most of the MOFs are insulators, due to the poor overlapping between the d orbitals of the metals and π orbital of the insulating organic ligands.

To benefit from both the versatility of MOFs' functionality and the electronic conduction of conducting polymer. We've synthesized porphyrinic zirconium metal–organic frameworks [MOF-525, $Zr_6O_4(OH)_4(TCPP\text{-}H_2)_3$, where porphyrin $H_4\text{-}TCPP\text{-}H_2$ = ($C_{48}H_{24}O_8N_4$)] nanocrystals. The MOF-525 possesses high surface area (theoretical value = 2620 $m^2\ g^{-1}$) with a unique microporous structure, which could contribute high EDLC performance. The synthesized MOF-525 particles were incorporated with conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) to improve the conductivity so as to enhance the capacitance performance. In this study, we designate composites as $MPP_{X\%}$, where X is the mass fraction of PEDOT:PSS added in the composite. X was varied from 0% to 15% depending on the amount of PEDOT:PSS loaded. The optimized supercapacitor shows an outstanding specific capacitance of 680 F g^{-1} (charging current density = 2 A g^{-1}, Fig. 1b). EDLC performance could be enhanced with high surface area MOF-525 and that both charge-discharge rate and charge transfer resistance were improved with the addition of conducting polymer (Fig. 1a, 1c).

To the best of our knowledge, this is the first report demonstrating MOF/conducting polymer composites as an electrode material in electric double layer capacitors (EDLCs) which simultaneously exhibit both high BET surface area (1424 $m^2\ g^{-1}$) and reasonably high electrical conductivity (Fig. 1a, 1c). The proposed composite material could be a promising candidate for EDLCs because it is easy to prepare high capacitance performance with good stability.

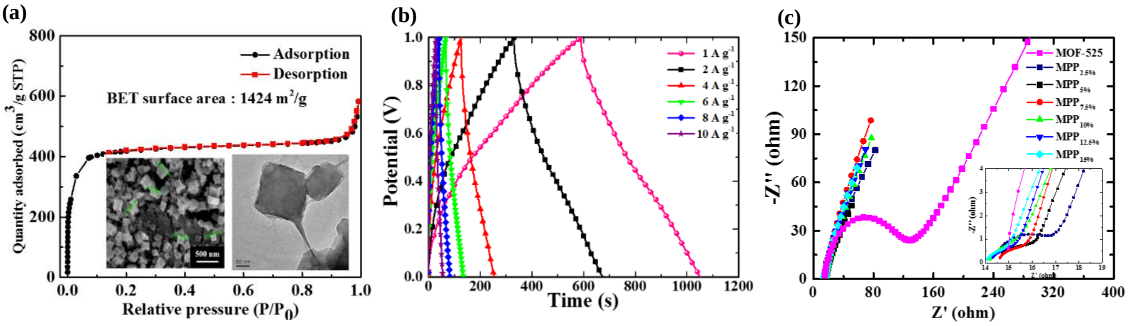

Fig. 1. (a) N_2 adsorption-desorption curves, SEM and TEM image of MPP, (b) galvanostatic charge/discharge curves of MPP nanocomposite at different current densities, (c) Nyquist plots of MOF-525 and MPP nanocomposites.

Electrochemical Preparation and Photogenerated Cathodic Protection Property of β-Bi_2O_3/TiO_2 Nanotube Composite Film

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Stainless steel is one of the most important engineering materials owning to its excellent corrosion resistance, mechanical and processing properties. But it is still faced with the threat of localized corrosion in many environments. Recently, a new strategy known as photogenerated cathodic protection was developed to suppress metal corrosion. In a photogenerated cathodic protection system, the electrons generated in the photoanode under illumination are transferred to the coupled metal, thus, the metal potential shifts negatively and the corrosion is rightly inhibited. As the first used photoanode material, TiO_2 has drawn extensive attentions because of its advantages, such as abundance, low toxicity, and high stability. However, it also has natural drawbacks such as wide bandgap and fast recombination of photogenerated electron-hole pairs, which are apparently detrimental to photoresponse performances. So the modification of a TiO_2 film is necessary to improve its photocathodic protection effect. Bismuth oxide is a widely used photocatalyst due to its unique optical and electrical properties. It is found that β-Bi_2O_3 has a narrow bandgap (~2.3 eV) and excellent photoresponse in visible light region, which makes it a good candidate to modify TiO_2 and enhance the photoelectrochemical anticorrosion effect.

In this work, TiO_2 nanotube (TiO_2-NT) films were fabricated on Ti foils by anodic oxidation conducted by a two-electrode system in an aqueous solution of HF. After the anodization, the amorphous TiO_2 nanotubes were crystallized by annealing at 450°C for 2 h. Then, β-Bi_2O_3 nanoparticles were deposited onto the TiO_2-NT surfaces by an ultrasonic assisted pulse electrodeposition method. Prior to the electrodeposition, the TiO_2-NT film was immersed in a solution containing $Bi(NO_3)_3$, HCl and EDTA under ultrasonication. The pulse electrodeposition was carried out by a traditional three-electrode system with the TiO_2-NT film as the working electrode, a SCE as the reference electrode and a Pt foil as the counter electrode. The electrolyte for pulse electrodeposition was the same as the solution used for ultrasonication treatment. And the procedure of ultrasonication and electrodeposition was repeated a certain number of times to obtain the desired β-Bi_2O_3/TiO_2 nanotube film. After deposition, the prepared film was annealed at 550°C for 2 h. The properties of the prepared film were characterized by SEM, EDX, XRD, XPS, UV-Vis and FL spectroscopy, and photoelectrochemical measurements.

The SEM results showed that the prepared TiO_2-NT film was composed of highly ordered nanotubes with the average inner diameter of 100 nm, wall thickness of 15 nm and length of 300 nm. The analyses of EDX, XRD and XPS confirmed that the β-Bi_2O_3 nanoparticles were successfully prepared on the TiO_2-NT film by the ultrasonic assisted pulse electrodeposition method. The photoresponse of β-Bi_2O_3/TiO_2 composite film was indeed enhanced and its light absorption range was broadened to the visible region according to the UV-Vis and FL spectroscopy measurements. The Bi modified TiO_2-NT film by forming Bi-O-Ti bonds to introduce a localized impurity level within the band gap, which would narrow the bandgap of TiO_2-NT film and extend the photoabsorption region. The composite film showed greater photocurrent than a pure TiO_2-NT film in a 1 M KOH solution. This was mainly due to the narrowing of bandgap and the formation of the p-n heterojunction structure, which can effectively promote the separation of photo-generated electron-hole pairs. Finally, and most importantly, the modified composite film under white light illumination showed an effective photogenerated cathodic protection for 403 stainless steel in a 0.5 M NaCl solution.

Acknowledgements

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Development of Metallic Bipolar Plate for PEFC by Coating Carbon Thin Film on Stainless Steel

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Introduction : The polymer electrolyte fuel cell (PEFC) has characteristics that it can operate at a relatively low temperature and can be downsized. Therefore, development is proceeding in a wide field such as a stationary power supply and a power supply for electric vehicles. It is required to reduce the size and weight of the fuel cell as well as to lower the price. For example, it is a method to solve by changing the separator material from a conventional carbon material to a metal material.

In this study, we proposed the following method aiming at the development of simple and low cost production method. The method is to coat the surface of stainless steel with a resin thin film and then carbonize it at low temperature. We investigated the structure of the carbon surface and the properties as a separator material.

Experimental method : Austenitic SUS304 stainless steel with various thickness was used without heat treatment. Surface pretreatment of the specimen was polished with wet emery paper up to #600. The resin coating on the specimen surface was carried out by electrodeposition coating method using various cationic paints (Nippon paint Co.). Electrodeposition coating was carried out with varying electrolytic voltage and time at 303K. Carbonization of the coated thin film was performed in an electric furnace under a nitrogen atmosphere. Sintering temperature was 673 K to 1173 K for 2 hrs. Chemical evaluation of carbonized thin film was carried out by measurement of electrical resistance, Raman spectroscopy, XPS, XRD, SEM, etc. Electrochemical properties were evaluated by measurement of the polarization curve. The polarization curves were measured by linear sweep voltammetry method at room temperature in 0.5 M H_2SO_4 solution by a three electrode system using a working(specimen) electrode, a platinum plate as a counter electrode and Hg/Hg_2SO_4 electrode as a reference electrode.

Results and discussion : Fig. 1 shows the relationship between the electric conductivity of the carbon film obtained by heat-treating the resin film formed on the specimen surface of various resin materials at 773 to 1173 K and sintering temperature. The electrical resistance of sintered film decreased with increasing heat treatment temperature. And it showed under 10 mΩ cm at 1073 K. In order to improve the electrical conductivity at lower temperature treatment, a coating was prepared by mixing various kinds of carbon powder with resin. As a result, even in the heat treatment at 873 K, a value of 10 mΩ·cm or less was obtained.

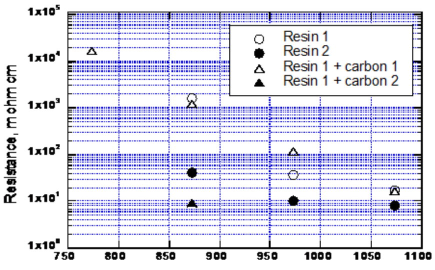

Fig. 1 Relationship between sintering temperature and electronic resistance of carbon film

Fig. 2 shows anodic polarization curves for stainless steel and covered by carbon coated specimens. The polarization curve of the untreated specimen showed an immersion potential of about 0.0 (V vs. SHE) and a passivation current density of 20μA/cm^2 similarly to the normal polarization curve. On the other hand, the immersion potential in all carbon-coated specimens was 0.6 to 0.8 (V vs. SHE) and shifted in the noble direction and the anode current became 10A/cm^2 or less. It was revealed that sufficient corrosion resistance and electric conductivity are exhibited by giving carbon coating treatment.

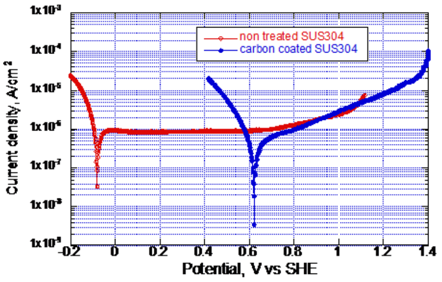

Fig.2 Polarization curves of non treated and carbon corted SUS304 specimens in 0.5M H_2SO_4 solution at room temperature

On that day, we will explain the relationship between electrodeposition coating using various cationic resins and the conductivity and corrosion resistance of the carbonized film. We also report on the power generation test using the prepared separator.

This research was partly supported by the NEDO.

Cobalt polypyridine complexes as redox electrolytes for ZnO-based dye-sensitized solar cells

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The increasing demand of green energy is pushing several research fields in exploring highly efficient technologies as alternative to common sources. Dye-sensitized solar cells (DSCs) represent a valid possibility to develop very inexpensive solar-to electrical energy conversion, but their limited efficiency is still under investigation. Among the components involved in the mechanisms of these devices, the redox shuttle plays a relevant role as regenerator of the photo-oxidized dye. Cobalt bipyridine complexes are currently explored as mediator in DSCs but suffer of higher recombination rate compared to I^-/I_3^- [1]. This aspect is more important in ZnO semiconductor-based solar cells which are known to have a lower recombination resistance than TiO_2 owing to the high electron mobility [2].

The contribution of our project to the research for high efficient and low costs DSCs is a scanning electrochemical microscopy (SECM) experiment on ZnO photoanodes. Bulky cobalt complexes such as $Co(bpy)_3(PF_6)_{2/3}$ that are used as redox shuttles in DSCs are employed as redox mediators for SECM. The trend of the hindrance of mass transport by the steric shuttle can affect dye regeneration and injected electrons recombination from the conductive band of the semiconductor by Co(III). The dependence of diffusion on mesoporous film porosity and thickness is evaluated for cobalt redox couples. It uses a systematic study of ZnO photoanodes with different tunable features. The suppression of back electron transfer from ZnO to the oxidize form of the mediator is analyzed by tuning the compact blocking layer thickness and by adding lithium salts and other cations such as 4-tert-butylpyridine to the electrolytic solution.

We refined the choice of all-organic class of sensitizing dyes well known in literature, for instance DN216 and D35, adsorbed on the photoanode to ensure lasting and stable sensitization of the cell. Loss processes that decrease the efficiency of nanostructured ZnO-based cells are analyzed with scanning electrochemical microscopy (SECM) [3-4] and common electrochemical characterizations. The photocurrent generated at the sensitized anode is measured with a picoammeter connected to a computer-controlled switch. During SECM characterizations, the overall flux from the DSC is monitored in short circuit conditions and open circuit conditions.

Literature:

[1] S. M. Feldt, G. Wang, G. Boschloo, A. Hagfeldt, J. Phys. Chem. C **2011**, 115, 21500–21507.
[2] J. A. Anta, E. Guillén, R. Tena-Zaera, J. Phys. Chem. C **2012**, 116, 11413−11425.
[3] Y. Shen, K. Nonomura, D. Schlettwein, C. Zhao, G. Wittstock, Chem. Eur. J. **2006**, 12, 5832–5839
[4] Y. Shen, U. M. Tefashe, K. Nonomura, T. Loewenstein, D. Schlettwein, G. Wittstock, Electrochim. Acta **2009**, 55, 458–464

Controlled synthesis and CO_2 photoelectroreduction activity of conducting polymer/SiC hybrid nanostructures

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A promising method to reduce atmospheric carbon dioxide concentration may be the photoelectrochemical (PEC) reduction of CO_2, where carbon dioxide is reduced to fuels and other valuable products. In such procedures CO_2 is converted by photoactive materials (semiconductors) utilizing the energy of sunlight. CO_2-reduction is a multi-electron process with considerable kinetic barriers, thus it requires the use of carefully designed photocathode materials to reduce CO_2 economically viable with high efficiency. In addition, the photoelectrode has to meet several requirements (narrow bandgap, appropriate band edge positions, efficient charge carrier transport, good surface charge transfer kinetics, chemical/electrochemical/photo-stability, low toxicity, favorable price) to operate in a sustainable manner. A single material cannot fulfil all these criteria at the moment, thus it is needed to synthesize hybrid materials, to exploit the potential synergies resulting from the nanocomposite formation.

In this work, we present the electrochemical and photoelectrochemical synthesis of SiC-based, polyaniline and poly(3,4-ethylenedioxythiophene) containing hybrid nanocomposites. The amount of the deposited conducting polymer was controlled by the polymerization charge density in the case of the electrochemical synthesis; in the photocatalytic method the thickness was controlled simply by changing the irradiation time. The composition, structure and the morphology of the synthesized nanostructures were characterized by UV-vis and Raman spectroscopy, thermogravimetric analysis, transmission- and scanning electron microscopy. The electrochemical and the photoelectrochemical behavior of the synthesized hybrid films was examined by cyclic voltammetry and linear sweep photovoltammetry. Long term constant-potential electrolysis was also performed and the formed products were analyzed using GC.

The most important outcome of this study is that we proved that the hybrid materials show an improved photo-electrocatalytic activity compared to the components separately.

Solution combustion synthesis of $CuCrO_2$ and application for CO_2 reduction

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The continuously growing concentration of atmospheric carbon dioxide necessitates urgent actions. Solar fuel generation is an attractive approach, because in addition to the reduction of the carbon dioxide quantity, fuels can be produced in this process. For the photoelectrochemical reduction of CO_2, p-type semiconductor electrodes are required. Oxide semiconductor photocathodes are eminently attractive candidates in this manner.

One of the mostly studied materials in this vein is Cu_2O, which shows excellent performance in this process. However, the lack of its long-term stability hinders its application. Therefore, a more stable class of semiconductors with the chemical structure of $CuXO_2$ (where X: Fe^{3+},Cr^{3+},Rh^{3+},Al^{3+} etc.) attracts significant interest nowadays. Based on their conduction band edge position, they have the potential for carbon dioxide reduction. In addition, the bandgap of these materials (which is between 1.3-3.0 eV) can be tuned by the changing the synthesis conditions (and thus the exact stoichiometry).

These materials are usually prepared by solid state reactions which demand lots of energy and time. There are some methods which aim to decrease the amount of energy during the synthesis. However, these methods are usually not time efficient. On the other hand, solution combustion synthesis (SCS) is a low cost and rapid synthesis for these materials. In this reaction the precursor metal-nitrate will react with the fuel (i.e., urea, glycine, or hexamethlyenetetramine) and as a result of the highly exothermic reaction the product will be crystalline. With this method the composition of product, porosity, crystallinity can be changed by changing the fuel / oxidizer ratio.

On my poster, I will present the effect of different synthesis conditions and how to change the composition and properties of $CuCrO_2$. The as-synthesized $CuCrO_2$ will be characterized by XRD, Raman spectroscopy, TG, EDX, SEM, TEM, and electrochemical methods. Finally, we show that the $CuCrO_2$ is capable to reduce the CO_2 in a photoelectrochemical cell.

Electroless Platinum Deposition using Multivalent Metal Ions or Hydrazine as Reducing Agents

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Two new type electroless plating processes for deposition of continuous platinum layer are proposed and compared with known process of electroless platinum deposition using hydrazine as reducing agent.

In this study investigation of the kinetics of electroless Pt deposition, using reducing agents such as Co(II)/Co(III) and Ti(III)/Ti(IV) redox systems, is presented. The Pt layers were deposited on the copper or nickel surfaces. The morphology of Pt layers deposited using different reducing agents was investigated by means of Field Emission Scanning Electron Microscopy (FESEM). Kinetics of deposition rate of Pt was investigated by means of the Electrochemical Quartz Crystal Microgravimetry (EQCM). It was found that the deaeration of the electroless Pt plating solutions with argon, using Co(II)/Co(III) or Ti(III)/Ti(IV) redox systems as reducing agents, results in higher deposition rates of Pt. When using Co(II)/Co(III) redox system as a reducing agent, the rate of electroless deposition of Pt is ca. 0.3 µg cm^{-2} min^{-1} when using Ar-deaerated plating solution, whereas the one in non-deaerated plating solution is significantly lower, e.g. 0.02 µg cm^{-2} min^{-1}. When, using the Ti(III)/Ti(IV) redox system as reducing agent, the Pt deposition rate in Ar-deaerated plating solution is higher compared with that using CoII)/Co(III) redox couple. It should be noted that the obtained Pt layers deposited on the surface of Cu using Co(II)/Co(III) or Ti(III)/Ti(IV) redox pairs as reducing agents are continuous and compact. The kinetic data of the mentioned reactions is discussed and compared with that obtained using hydrazine as reducing agent.

Acknowledgment

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Electrospun PVdF Nano Fiber Web as Separator for Lithium Ion Batteries

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Electrospun nanofiber web is highly attractive as a separator for lithium ion batteries because of its high electrical, thermal, chemical and mechanical properties. In moving toward wider battery applications of the nanofiber separator, a deeper understanding on the structure and property relationship is highly meaningful. In this regard, we prepared electrospun poly(vinylidene fluoride) (PVdF) webs with various thickness (10~100 μm) and investigated their electrochemical performances. As the thickness of the web was decreased, a decrease of porosity and an increase of pore size were resulted in. Also, the thinner separators exhibit faster electrolyte wetting and smaller interfacial resistance. However, the discharge capacity, rate capability, cycling stability, and temperature stability were highest at an intermediate thickness of 30 μm, stressing the importance of absolute amount of electrolyte uptake.

References

1. H. R. Jung, D.H. Ju, W.J. Lee, X. Zhang, R. Kotek, Electrochim. Acta 54, 3630 (**2009**).

Fabrication and Characterization of All Solid–State PEO/LLZO composite electrolytes for high performance lithium ion batteries

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We present the fabrication of a composite electrolyte for solid state batteries consisting of Al-substituted $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic particles dispersed in a Poly (ethylene oxide) matrix. The Al- substituted cubic garnet like LLZO solid state ceramic ion conductor is obtained by modified Pechini method. Homogeneous composite electrolytes with different ceramic/polymer composition ratio were obtained by solution casting. The results show that LLZO particles have a positive effect on the ionic conductivity, electrochemical stability. Among the PEO/LLZO composite electrolyte, the composite electrolyte containing 45wt% LLZO was found to exhibit a maximum ionic conductivity of 5.8×10^{-4} Scm-1 and electrochemical window of 0-6V at 70℃. All solid state battery NCM622/L was fabricated and presents fascinating electrochemical performance with attractive capacities of 175, 167, 148, 81 mAh/g and at current rates of 0.1, 0.2, 0.5 and 1C, respectively at 70℃.

Electrodeposition of Silver Nanoparticle on Flower-like Bi_2WO_6 Decorated Metal Wire-mesh and their Application as Visible Light Driven Photocatalysts

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Bi_2WO_6 is an effective photocatalyst for the degradation of harmful compounds or pollutant. In this study, flower-like Bi_2WO_6 were grown on stainless-steel wire-mesh by a hydrothermal method. Then, silver nanoparticles were uniformly grown on flower-like Bi_2WO_6 by a double-potentiostatic electrodeposition method which included the nucleation and growth processes. Flower-like Bi_2WO_6 exhibited good photocatalytic activity. Bi_2WO_6 decorated wire-mesh showed improved activity. Because of the close interfacial contact between Bi_2WO_6 and conductive stainless-steel wire-mesh, strong electronic interaction can be achieved and enhance the separation of photogenerated carriers. The spacial distribution and size of silver nanoparticles on the wire-mesh were tuned by changing the applied voltage and deposition time for the electrodeposition method. The Ag-Bi_2WO_6-wire mesh exhibited high visible light driven activity. The improved charge separation and optical absorption were confirmed by the results of photoluminescence spectroscopy, photocurrent test, electrochemical impedance spectra, and UV–vis diffuse reflection spectroscopy. The surface morphology, surface chemistry, and crystalline property of the photocatalysts were investigated by X-ray diffraction, scanning electron microscope, transmission electron microscopy and X-ray photoelectron spectroscopy. The reusability of the recycled photocatalyst will also be investigated.

Electrochemical characteristics of graphite felt electrode by surface modifaction for VRFBs

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Recently, there have been a lot of research in vanadium redox flow battery (VRFB) which is used as a large scale energy storage system and power supplier. Especially, graphite electrodes play an important role because they do directly act as electrochemical reaction in cell.

In this study, commercial graphite felts were prepared by heat treatment in the range of 400 to 600 °C, controlling the condition of heat treatment such as air purity, heating processing time. As a result, the surface morphology and oxide of electrode were observed by SEM and XPS. Moreover, electrochemical evaluations such as CV (Cyclic Voltammetry) and impedance were performed in three electrode cell at room temperature, in which the kinetic properties of electrode were different with the condition of surface modification. Furthermore, small VRFB full cells constructed with the graphite felt showed the properties of charge and discharge profile corresponding to the above analysis and electrochemical test. Therefore, we will introduce the effect of heat treatment on the graphite felt electrode and its correlation in electrochemical reaction in more detail.

Fabrication of Ag_2S/TiO_2 Nanotube Film and Its Photoelectrochemical Anticorrosion Effect on Stainless Steel

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It is common knowledge that TiO_2 is a promising semiconductor with many advantages, which has been used in many applications. Especially in the area of corrosion control, TiO_2 films may provide photoelectrochemical anticorrosion effect (namely photocathodic protection) for metals. The fundamental principle of this new cathodic protection method is that the photogenerated electrons are transferred from a TiO_2 film to the coupled metal substrate, then the potential of the metal decreases to a more negative value and the metal corrosion is reduced. In order to improve the photoresponse performances and photocathodic protection effects of TiO_2 films, it is necessary to modify the films with other semiconductors. In the present work, Ag_2S was deposited on the TiO_2 nanotube film prepared by anodization for enhancing photoelectrochemical anticorrosion effect of the film.

TiO_2 nanotube films were prepared on Ti foils in a two-electrode cell holding an aqueous glycerol solution with 0.5 wt% NH_4F by anodic oxidation at 20 V for 30 min. After the anodization, the TiO_2 nanotube specimens were annealed at 450°C for 2 h. Ag_2S nanoparticles were deposited onto the TiO_2 nanotube film by a successive ionic layer adsorption and reaction method by immersing the film specimen in an aqueous alcohol solution with $AgNO_3$ and a methanol solution with Na_2S alternately. The prepared film was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and UV-Vis spectroscopy, and the photocathodic protection effect of the film was investigated by photoelectrochemical measurements.

The results indicated that the prepared TiO_2 film was composed of ordered nanotubes, the average inner diameter, wall thickness, and length of the nanotubes were about 100 nm, 15 nm and 1200 nm, respectively. The surface analyses showed that Ag_2S nanoparticles were successfully deposited on the nanotube surfaces, the film still retained the ordered nanotube appearance, but the nanotube surfaces became rough, which was helpful to enhanced visible light photoelectrochemical performances of the Ag_2S/TiO_2 composite film. After modifying the TiO_2 film with Ag_2S nanoparticles, the photoresponse of Ag_2S/TiO_2 composite film was extended into the visible light region, and its photoabsorption property was greatly improved. The photocurrent of the composite film was greater than that of the pure TiO_2 nanotube film in a 0.2 M NaOH + 0.1 M Na_2S mixed solution. The Ag_2S/TiO_2 composite film had a better photocathodic protection effect on the 403 stainless steel than the pure TiO_2 nanotube film. When 403 stainless steel in a 0.5 M NaCl solution was coupled to the Ag_2S/TiO_2 composite film in a photoelectrochemical cell under white light illumination, its potential decreased by about 600 mv, showing an effective photoelectrochemical anticorrosion effect for the steel.

Acknowledgements

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Influence of pulse period of PR plating on the properties of electrodeposited coatings of gold

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Electrodeposited coatings of gold have more excellent properties, and the coatings’ thickness can be reached to 150μm. The main system is cyanide or sulfite system. Our project team developed a new cyanide-free electroplating system, which combined with PR power. Combination of different parameters has different effect on electrodeposited coatings of gold. On the basis of cyanide-free electroplating process, we had a study on the effect of pulse period on the properties of electrodeposited coatings of gold using PR voltage power. In this paper, we got different electrodeposited coatings of gold after 24h as our samples, whose experiment condition took pulse period as a single variable. To have a better microcosmic surface view, we took some SEM images. We also had a contrastive analysis of orient of crystal of different electrodeposited coatings of gold using XRD method. Different deposition conditions will result in different hardness of electrodeposited coatings of gold, which can measure by Vickers Indenter. Through single variable experiment, which the pulse period was treated as a single variable, we found different pulse period can result in different properties, including SEM microcosmic surface view (as follows in figure 1), average crystal size, and Vickers hardness. Finally, the Vickers hardness of electrodeposited coatings of gold was higher, and could reach to 100HV, when pulse period was 45ms or 60ms.

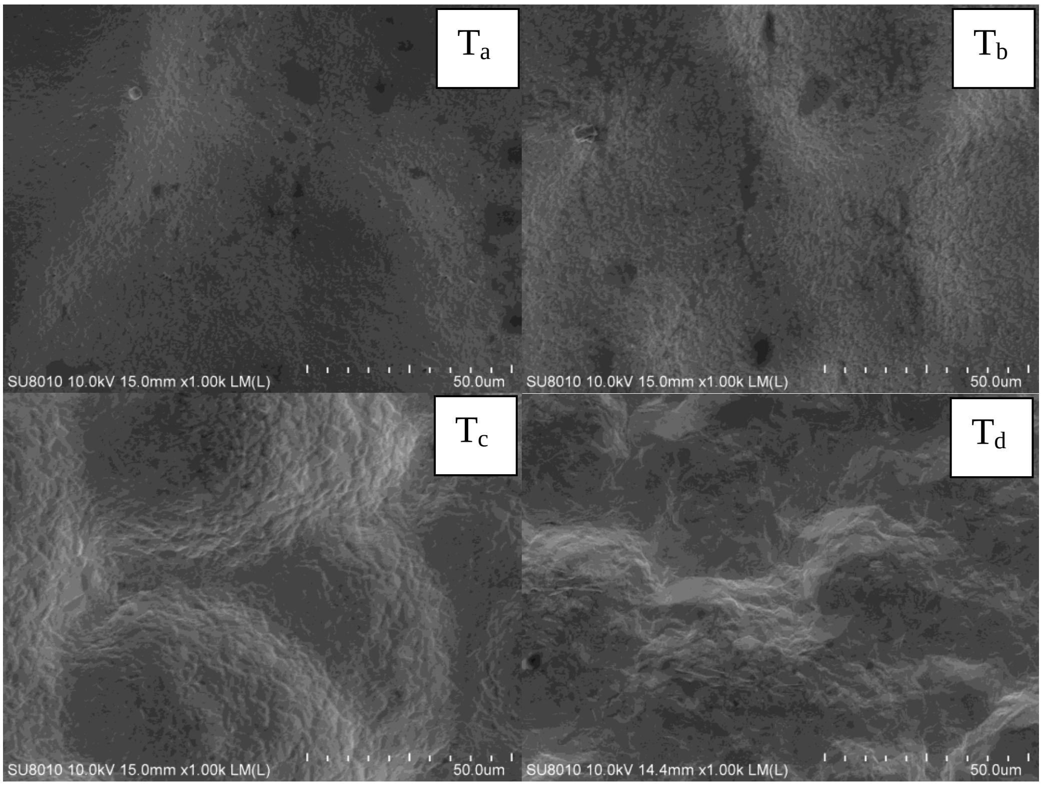

Figure 1The SEM surface view of different electrodeposited coatings using different cycle of electrical pulse（Ta=60,Tb=45,Tc=30,Td=15）

In Situ Detecting of Visible-Light-Driven Water Oxidation Intermediates at Nanostructured $BiVO_4$ Adsorbed at Micropipette based Liquid-Liquid Interface

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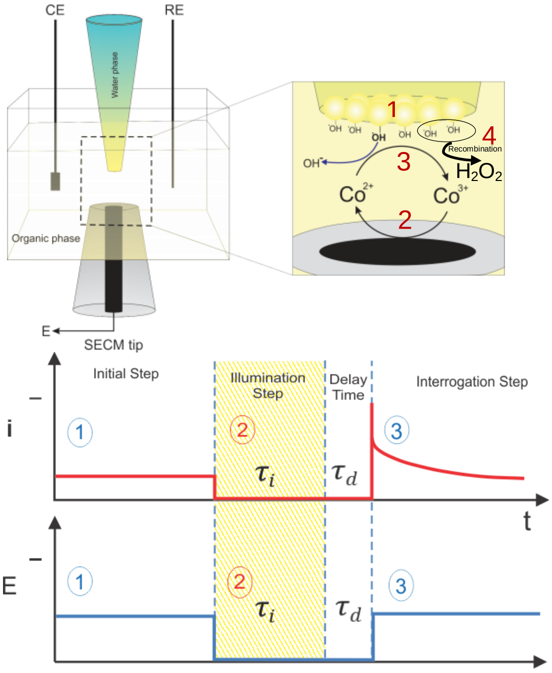

Polarizable liquid/liquid (L/L) interface represents molecularly sharp platform suitable for assembling of nanostructured semiconductor photocatalysts which have been proposed as a novel approach, generating charge careers (electron-holes pair) reactants in either side of interface, involving in photo-induced charge transfer reactions at liquid-solid-liquid boundaries. The pathway and efficiency of this interfacial reaction could be controlled easily by polarization of interface either electrochemically or chemically. This unique possibility of L/L interface system is fully desirable in design of artificial photosynthesis systems based on photocatalyst for efficient water splitting reaction, which is currently a hot topic in solving the energy challenges with minimal environmental impact. $[Co(bpy)_3](PF_6)_3$ soluble in organic phase used here not only as a probe of SECM analysis, but also as a sacrificial agent, which can effectively improve the separation efficiency of photogenerated charges at the hyperbranched nanostructured $BiVO_4$ modified interface, yielding to higher amount of O_2 as a main product of water oxidation reaction (WOR) by photogenerated holes in $BiVO_4$.[1] The high surface area of nanosized $BiVO_4$ crystals with a specific hyperbranched structure [2] along with the defect free liquid/liquid (L/L) interface could overcome the inherent poor electron transport properties of $BiVO_4$ materials. Coupling of Liquid/Liquid (L/L) Interface with Surface Interrogation-Scanning Electrochemical Microscopy (SI-SECM) proposes novel insight to study the photo-induced water oxidation reactions on $BiVO_4$ based material as visible light-responsive photocatalysts. Herein, SI-SECM[3] is used for the detection, quantification and evaluation of decay kinetics of adsorbates intermediates generated photochemically at the surface of nanocrystaline $BiVO_4$ substrate. Accordingly, nanocrystaline $BiVO_4$ at L/L interface at tip of micropipette (5 µm diameter), illuminated with visible light (λ > 420 nm) while adsorbates are produced on the $BiVO_4$ surfaces (1 in Figure). On the interrogation step, the sensing mechanism consists of in situ generation, at an interrogator electrode of gold microelectrode (ME), of a titrant (Co^{2+}) from a reversible redox pair of Co^{3+} complex soluble in DCE phase that is able to react chemically with the radical adsorbed species on the $BiVO_4$ substrate and report the amounts of this adsorbates through the SECM feedback response in chronoamperometry mode (2 and 3 in Figure). At longer delay time, the net current, which is the difference amount of currents with and without light, decreases as expected, because more adsorbates are disappeared during recombination process of radicals intermediates at delay step (4 in Figure). By integrating this current over delay time, one can obtain useful quantitative information about the density amount of radicals per projected area of $BiVO_4$ (as small as ME) and decay kinetics of them. The results could give us novel insight and direction in design of appropriate photocatalyst based L/L interface system for WOR as a challenging step in water splitting process.

References:

(1) Rastgar, S.; Pilarski, M.; Wittstock, G. *Chem.Commun.* 2**016**, *52*, 11382-11385.
(2) Zhao, Y.; Xie, Y.; Zhu, X.; Yan, S.; Wang, S. *Chem. Eur. J.* **2008**, *14*, 1601-1606.
(3) Park, H. S.; Leonard, K. C.; Bard, A. J. *J. Phys. Chem. C* **2013**, *117*, 12093-12102.

Synthesis and Activity of Cobalt-Sulfide Electrocatalysts for Photoelectrochemical Water Splitting

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Recently, cobalt-based compounds such as (hydro)oxides, chalcogenides, phosphates, perovskites or molecular complexes have been identified as highly active materials for energy-related applications (water electrolysis, supercapacitors, dye-sensitized solar cells) [1–5]. Among these, cobalt-sulfide (denoted as Co–S) compounds have been found to have a considerable potential to be used as a counter electrode material in dye-sensitized solar cells (DSSC) or photocathode for photoelectrochemical hydrogen generation from aqueous solutions. The possibility of one-step electrodeposition of Co–S thin films using earth-abundant elements provides a particularly attractive alternative for the replacement of Pt or other noble metals. Depending on synthesis conditions one can obtain Co–S films of various morphology and structure (for instance, CoS, CoS_2, Co_9S_8, Co_4S_3) which are characterized by different photoelectrochemical activity.

The aim of this work was to prepare Co–S thin films on conductive glass substrates and to evaluate the influence of synthesis conditions on their structure, morphology and photoelectrocatalytic activity in hydrogen evolution reaction (HER).

Co–S films on FTO substrate were prepared by electrochemical deposition. The synthesis was carried out using a deposition bath containing mainly thiourea, cobalt chloride and a small amount of ammonia in order to maintain the neutral pH value of the electrolyte. 0.1 M potassium phosphate buffer solution (pH 7) was used as a supporting electrolyte for the photoelectrochemical measurements. Various electrochemical methods were used to characterize the performance of cobalt sulfide (Co–S) films in aqueous solutions. Structural and chemical characterization of the prepared films was carried out by means of scanning electron microscopy and energy dispersive spectroscopy, X-ray powder diffraction, X-ray photoelectron, Fourier transform infrared, atomic absorption and UV-Vis diffuse reflectance spectroscopy.

It has been determined that the synthesis conditions (electrodeposition potential, temperature and composition of the electrolysis bath, heat-treatment of electrocatalysts) significantly influences the structure and photoelectrocatalytic activity of the prepared films. The electrodeposition was proved to be scalable and versatile method for the synthesis of efficient functional Co–S films. The experimental results revealed that p-type Co–S catalysts are highly active and stable for hydrogen evolution reaction (HER) in pH 7 phosphate buffer solutions over prolonged operating time. The performance of active HER catalyst was confirmed by low values of overpotential featuring a Tafel slope of about 54 mV/decade. The obtained results provide a deeper understanding of the relationship structure-activity in HER for metal chalcogenide electrocatalysts.

References

1. D.K. Bediako, A.M. Ullman, D.G. Nocera. Topics in Current Chemistry (eds. H. Tuysuz, C.K. Chan). 371 (2016) 173.
2. K.K. Lee, W.S. Chin, C.H. Sow. J. Mater. Chem. A. 2 (2014) 17212.
3. S.K. Swami, N. Chaturvedi, A. Kumar, R. Kapoor, V. Dutta, J. Frey, T. Moehl, M. Grätzel, S. Mathew, M.K. Nazeeruddin. J. Power Sources. 275 (2015) 80.
4. Y. Sun, C. Liu, D.C. Grauer, J. Yano, J.R. Long, P. Yang, C.J. Chang. J. Am. Chem. Soc. 135 (2013) 17699.
5. J.Y. Lin, J.H. Liao, S.W. Chou. Electrochim. Acta. 56 (2011) 8818.

Pore sealing of porous low-k dielectrics assisted by self-assembled monolayers by 3-Aminopropyltrimethoxysilane treatment

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Highly porous low-*k* dielectric films with the dielectric constant less than 2.50 are needed for 32 nm and beyond technologies. In this study, plasma-enhanced chemical vapor deposition (PECVD) porous low-*k* dielectric films (k = 2.25) with open porosity of 32% and pore diameter as large as 1.15 nm were treated by 3-Aminopropyltrimethoxysilane (APTMS) in wet solution to form self-assembled monolayers (SAMs). The effects of SAMs on the electrical characteristics and reliability of highly porous low-*k* dielectric films are investigated. With SAMs formation onto the porous low-k film, both dielectric breakdown field and failure time were improved, but at the expense of a 17.5% increase in the dielectric constant and 1-order magnitude increase in the leakage current at 1 MV/cm. Moreover, the Cu barrier performance of highly porous low-*k* dielectric films can be enhanced by SAMs deposition. Therefore, this SAMs derived from APTMS is a promising method in pore-sealing and Cu barrier capability for highly porous low-*k* dielectric films.

1. A. Grill, S. M. Gates, T. E. Ryan, S. V. Nguyen, and D. Priyadarshini, *Appl. Phys. Rev*. **1** (2014) 011306.
2. F. Doniat, C. Anderson, C. Dussarrat, J. McAndrew , R. Opila, B. Wright, and D. Yang, *Microelectron. Eng*. **92** (2012) 34.
3. S. Armini, J. L. Prado, M. Krishtab, J. Swerts, P. Verdonck, J. Meersschaut , T. Conard , M. Blauw, H. Struyf, and M. R. Baklanov, *Microelectron. Eng*. **120** (2012) 240.
4. Y. M. Zhou, M. Z. He, and Z. Xie, *Appl. Surf. Sci*. **38** (2014) 353.

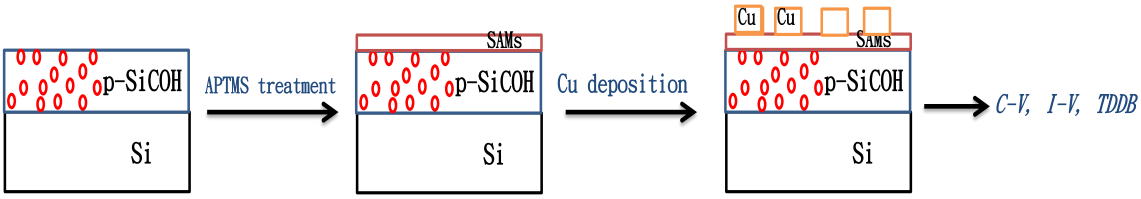

Fig. 1. **Experimental procedure in this study.**

Dependence of double-layer capacitance on the thickness of oxide layers deposited using atomic layer deposition

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Self-assembled monolayers cannot be used to readily prepare insulating layers that are a few nm thick and are pinhole-free onto electrodes. Here, atomic layer deposition (ALD) is used to prepare insulating oxide layers, whose thickness is controllable and which are pinhole-free toward electroactive species such as $Ru(NH_3)_6^{3+}$ and ferrocenemethanol, on indium tin oxide electrodes. The controllability of the uniform thickness of the oxide layers enables us to investigate the dependence of the total capacitance between an electrode and an electrolyte solution on the thickness of the ALD layer over a wide range of thicknesses. When the thickness is greater than ca. 2 nm, the total capacitance is dominated by only the ALD layer capacitance. Consequently, the reciprocal of the total capacitance is linearly proportional to the ALD layer thickness. From this finding, a schematic diagram for the potential profile across the ALD layer and in the electrolyte solution is proposed. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Photocatalytic Degradation of Methylene Blue by Doped TiO_2 Induced by Irradiation of Visible Light

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In contrast to monometallic catalysts, bimetallic-doped TiO_2 may exhibit synergetic effects on the photocatalytic activity. The bimetallic component strongly influences the photocatalytic activity; for example, (i) bimetallic doping would shift the optical response of the TiO_2-based catalyst from the UV to the visible region and (ii) it would improve electron–hole separation.

In literature, color removal of dyes was wildly used as an index to evaluate the catalytic activity of photocatalysts. In this study, photocatalytic decolorization of methylene blue (MB) was used as a probe reaction to evaluate the photocatalytic activity of the bimetallic-doped TiO_2.

In order to drive photocatalytic degradation reaction under visible light illumination, this study combined the technologies of Cu doping and Ag deposition to modify TiO_2 characteristics (called bimetallic-doped TiO_2), and the results have demonstrated the success of bimetallic-doped TiO_2 catalyst, which could degrade 90% of methylene blue with 10 mg/L initial concentration under visible light (430 nm) illumination after 10 min.

In this study, the combination between Ag and the Cu-doped/TiO_2 contributed to the enhancement of the light absorption of the synthesized material. The spectra indicate that the synthesized material with Ag deposition had an absorption in the region of visible light with an absorption edge around 430 nm. The UV–vis adsorption spectra also show that the light absorption ability of Ag-Cu/TiO_2 increased with increasing weight fraction of Ag in Ag-Cu/TiO_2 up to 10 wt% (Fig.1).

Deposition of Ag to Cu/TiO_2 increased the photo-sensibility of the latter and decreased the probability of electron–hole recombination, enhancing its photocatalytic activity. The prepared Ag–Cu/TiO_2 exhibited higher photocatalytic performance than the single dopant. The results could be a reference for the bimetal modification technology of photocatalytic.

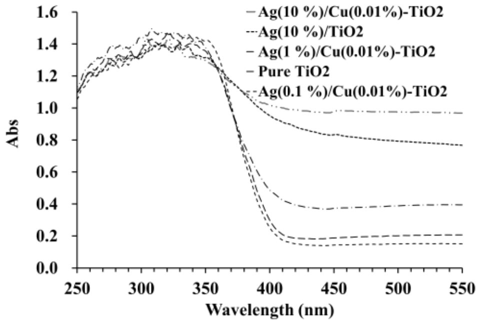

Fig.1 Comparison of UV–vis spectra for different bimetallic-doped catalysts.

Preparation and Characterization of Au-Cu Alloy Films for MEMS Accelerometer

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Au materials are commonly used as contact materials for high reliability circuit boards, electrical connectors, relays, and micro- and nano-scale electronic components because of their high electrical conductivity, chemical stability, corrosion resistance, and ductility. In recent years, Au has become a promising material to be used as the movable structures and proof mass in MEMS accelerometer, because the Au density is about 10 times higher than that of conventional Si. However, Au is known to be a soft material. Yield stress of bulk Au is reported to be 55~200 MPa [1]. On the other hand, it is recognized that the deformation of high-purity, single-component nanocrystalline materials can be compromised by grain growth even at room temperature. The mechanical strength and grain growth become critical concern in miniaturization of the pure Au-based MEMS accelerometer. Alloying of Au is expected to further enhance the mechanical stress and suppress the grain growth.

In this study, Au-Cu alloy films were fabricated by pulse electroplating. Grain size of Au-Cu alloy was ranged from 5.6 to 8.7 nm by changing the pulse peak current density (I_p) from 3 to 10 mA/cm^2, as shown in Figure 1(a). Grain refinement was attributed to the higher I_p, because main factors for formation of new crystals, such as high adatoms population and high overpotential can be achieved by applying higher I_p. The Cu content increased from 5.4 to 21.0 wt.% with increasing I_p. It should be noted that under the same current density, the Cu content of Au-Cu alloy film prepared by pulse electroplating was much lower than that prepared by constant current electroplating, which was attributed to and galvanic displacement of Au (the dissolution of Cu) during the pulse off-time. Lower Cu content is advantageous for the MEMS accelerometer, because lower Cu content implies higher density of Au-Cu alloy.

The components used in MEMS devices are usually in micro-scale, and mechanical properties of the materials in micro-scale are different from those of the bulk materials. Therefore, micro-mechanical properties of Au-Cu films were evaluated by micro-compression tests. The ultra-high compressive stress of 1200 MPa was achieved due to its ultra-fine grain and chemical composition change of Au-Cu alloy.

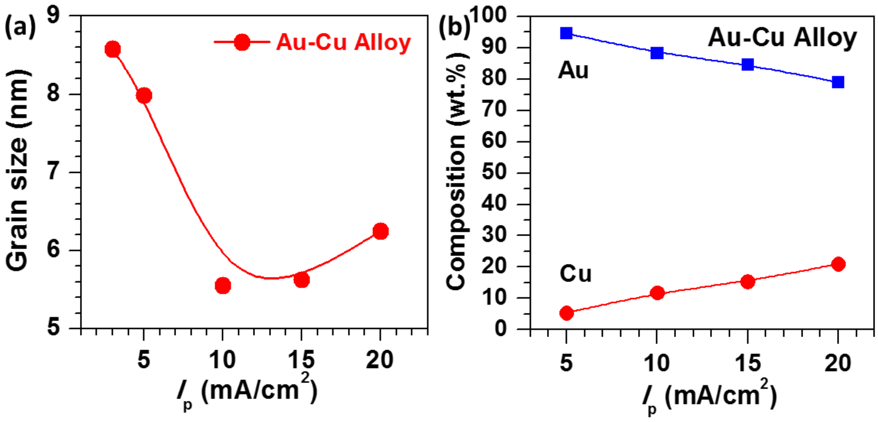

Figure 1(a) the pulse peak current density dependence on (a) grain size and (b) chemical composition of Au-Cu alloys.

Reference:
[1] H.D. Espinosa, B.C. Prorok, B. Peng, *J. Mech. Phys. Solid* **52** (2004) 667.

Photo characteristics of Electrodeposited CZTSe Thin Films on Different Substrates

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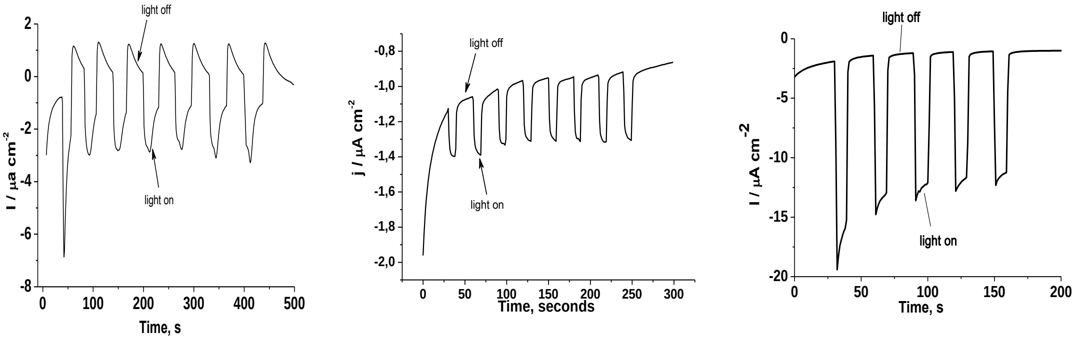
CZTSe and CZT(S,Se) films on different substrates were obtained electrochemically by deposition followed by selenization and sulfurization. Photoelectrical characteristics of the obtained films were studied and PEC results were compared.

The one-stage electrodeposition of **CZTSe** films was conducted by the method of potentiostatic electrolysis, E=-0.6V from the electrolyte based on 0.1M tartaric acid ($H_2C_4H_4O_6$), containing 0.005M $CuSO_4{*}5H_2O$, 0.01M $ZnSO_4{*}7H_2O$, 0.01M $SnCl_4{*}5H_2O$ and 0.005M $NaHSeO_3$, with pH=1.51.

The second procedure of obtaining **CZTSe** films included layer-wise electrochemical deposition of Cu/Sn/Cu/Zn precursors on a tantalum substrate and the subsequent selenization to form CZTSe film. The electrolyte solutions containing $CuSO_4$, $ZnSO_4$ and $SnSO_4$ were prepared using deionized water and sodium citrate, and the pH of solutions was controlled by means of H_2SO_4. The preliminary annealing of deposited Cu-Zn-Sn precursors was carried out in 95 % Ar+5 % H_2 at 350 °C during 30 min, after which the selenization of annealed Cu-Zn-Sn precursors was conducted in a quartz container (12.5 cm^3) with 5mg powdery Se at 1 bar pressure of Ar gas and 580 °C temperature.

To obtain a five-component **CZTSe(S)**compound, **CZTS** films were first deposited from the electrolyte based on 0.2M sodium citrate ($Na_3C_6H_5O_7$) with the addition of 0.1M tartaric acid ($H_2C_4H_4O_6$) and containing $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $SnSO_4$, $Na_2S_2O_3$ salts of analytically pure grade. The electrolysis was carried out at a constant potential of -1.0V during 30 minutes at a room temperature, and the selenization was carried out in a quartz container (12.5 $см^3$) with 5 mg powdery Se at 1 bar pressure of Ar gas and 550 °C temperature during 60 min.

The investigation of photoelectrical characteristics was carried от by PEC method using Gill AC potentiostat-galvanostat in a three-electrode quartz cell, in which **CZTSe/Mo, CZTSe/Ta** and **CZT(S,Se)/Mo** samples were a working electrode and a platinum spiral was a counter electrode. Ag/AgCl saturated with KCl was used as a reference electrode. Photocurrents were recorded in a darkness-lighting (light off/light on) mode from 0.1M sodium sulfate solution.



CZTSe/Mo CZTSe/Ta CZTSe(S)/Mo

Figure – The dependence of photocurrent on time according to PEC method

The comparison of results obtained with the films on different substrates shows that all the electrodeposited films have *p*-type conductivity. It has been as curtained that for CZT(S,Se) films obtained after selenization the value of photocurrents is considerably higher.

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Batch injection analysis for amperometric determination of ascorbic acid at ruthenium dioxide screen printed electrodes

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The use of sensors in field analysis has encouraged the development of new technologies and more suitable methodologies. Batch injection analysis (BIA) is a non- flow injection-based technique where a small liquid sample is injected from a micropipette tip toward a nearby detector surface, which is immersed in a large- volume, stirred blank solution. The detector records a transient, peak-shaped response that reflects the passage of the sample zone over its surface. The magnitude of the peak thus reflects the concentration of the injected analyte. Such dynamic measurements performed under batch operation yield an analytical performance similar to that observed under well-established FIA conditions [1].
BIA combined with screen printed electrodes (SPE) has demonstrated to be a portable electroanalytical system that can be used in the development of multiple analytical methods. It is a simple and robust system that allows to perform automated analysis with high reproducibility and versatility.

In the present work, the BIA cell coupled with a portable potentiostat has been used for amperometric determination of ascorbic acid in orange juices, using ruthenium dioxide (RuO_2) SPEs.

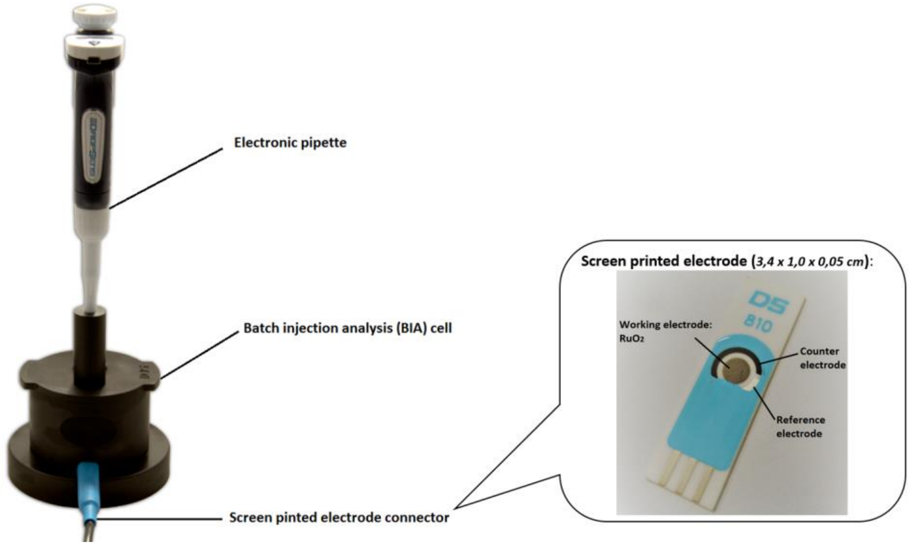

Figure 1: BIA cell and screen printed electrode used in the present work.

The injector is an electronic micropipette, where the tip is place in close proximity to the surface of the RuO_2 SPE. The dispensing conditions have been optimized and the pipette is programmed to dispense aliquots of 40 µL automatically every 70 seconds. A stirrer placed in the top of the cell, allows the dispersion of the sample over the entire cell volume. The sensor responds linearly to ascorbic acid in the range 0.01 – 1 mM (PBS 0.04M pH 7.4, $r^2 > 0.99$). The system was used to determine ascorbic acid in different orange juices brands, showing to be a rapid and simple method with an adequate analytical performance.

[1] J. Wang, Z. Taha, Anal. Chem. 1991, 63, 1053 – 1056.

The Correlation between Electrochemical Impedance Spectra and Morphology of KOH-Functionalized "Papers" in Supercapacitors

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Supercapacitors, also known as electrochemical capacitors, have recently gained increasing interest as alternative energy conversion and storage devices that can be complimented with batteries (1). They bridge the energy/power gap between dielectric capacitors and fuel cells/batteries, to supply high pulse power within a few milliseconds (2). In this study, we focus on activated carbon materials and the major role of morphology in delivering good electrochemical performance in supercapacitors.

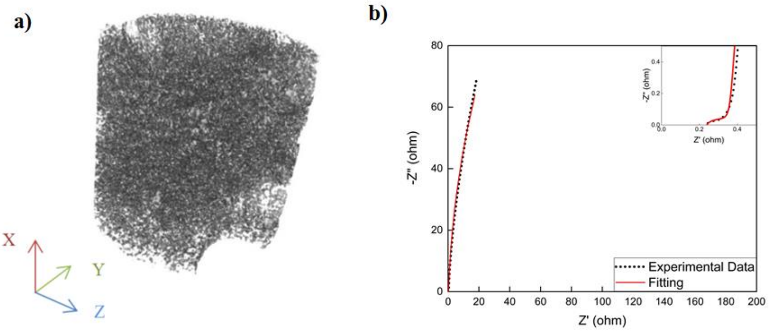

Figure 1: a) 3D reconstruction of KOH-activated cellulose obtained via x-ray tomography and b) corresponding electrochemical impedance spectrum with suggested model fitting.

Activated carbons, in various forms, are considered the primary candidate for electrode materials in electrical double layer capacitors due to their versatile properties that include good electronic conductivities, high specific surface areas and wide pore size distributions (3). Herein, the fine-tuning of pores through the activation of carbon with potassium hydroxide (KOH) has been implemented using different KOH/cellulose precursor ratios. The synthesized porous materials have been investigated for optimized performance. The effect of each of the porosity, tortuosity and pore size distribution on the electrochemical impedance spectroscopy has been studied. A simple equivalent series circuit consisting of the different resistive elements' contributions in the porous electrode was then suggested. This work has been coupled with different analytical characterization techniques including x-ray tomography along with electrochemical measurements to address the correlation between the porous structure of carbon electrodes and different relaxation times governed by the equivalent resistive components over a wide range of frequencies.

References

1. Conway BE, "Electrochemical supercapacitors: scientific fundamentals and technological applications," Springer Science & Business Media; 2013.
2. Wang G, Zhang L, Zhang J, "A review of electrode materials for electrochemical supercapacitors," Chemical Society Reviews, V. 41, No. 2, 2012, pp. 797-828.
3. Pandolfo AG, Hollenkamp AF, "Carbon properties and their role in supercapacitors," Journal of Power Sources, V. 157, No. 1, 2006, pp. 11-27.

Photoelectrochemical Aptasensors for the Detection of Antibiotics

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Photoelectrochemical (PEC) sensors have attracted considerable interest due to their inherent simple instrument and high sensitivity.[1] Photoactive species play important roles in PEC sensing process since they are employed to convert photoirradiation to electrical signal. Various n-type semiconductors have been introduced to fabricate photoelectrodes (photoanodes), and recently, p-type semiconductors have also been extensively explored to prepare photoelectrodes (photocathodes) that can generate cathodic photocurrent under photoirradiation. On another hand, aptamers (single-stranded oligonucleotides with specific sequences) have been employed as recognition elements in PEC sensors due to the advantages of high specific binding ability, wide target range, and acceptable stability. Todate, antibiotics have been commonly used to treat livestock bacterial infections due to their low cost and effective antimicrobial properties. However, excessive residual of antibiotics in the environment can exert toxic effects and cause antibiotic resistance. Hence, it is highly desired to develop sensitive and selective methods to quantitation of antibiotics at low concentrations. Herein, photoelectrochemical aptasensors for the detection of antibiotics were developed using photoanode or photocathode.[2,3]

Firstly, we developed a visible-light driven photoelectrochemical aptasensing platform for sulfadimethoxine (SDM) detection, using graphene (G)-doped Bi_2S_3 nanorods as photoanode. The photocurrent response of Bi_2S_3 was obviously increased after the doping of suitable amount of G. The recognition element, 5’-amino-terminated SDM-binding aptamer, was covalently immobilized on electrode. Based on the specific interaction between SDM and the aptamer, a PEC sensor responsive to SDM was obtained. Under optimal conditions, the proposed sensor showed a linear increased photocurrent response to SDM in the concentration range of 1.0-100 nM (Figure 1A), with a low detection limit (3S/N) of 0.55 nM. The practical feasibility of the PEC aptasensor was confirmed by measuring SDM in drug formulation and milk. Secondly, a novel cathodic “signal-off” strategy was proposed for PEC aptasensing of oxytetracycline (OTC). The fabrication process of aptasensor and the proposed sensing mechanism were illustrated in Figure 1B. P-type semiconductor BiOI doped with G modified electrode was employed as photocathode and OTC-binding aptamer was introduced as a recognition element. As a result, a stable cathodic photocurrent response was generated under a bias potential of -0.1 V (versus saturated calomel electrode), which was induced by the reduction of dissolved oxygen on the working electrode surface. While the analyte OTC was captured by aptamer, the formation of aptamer-analyte complexes led to the increment in steric hindrance for diffusion of electron acceptor to electrode surface, resulting in the drastic decrement of the cathodic photocurrent. Under the optimized conditions, the photocurrent response of the aptasensor was linearly proportional to the concentration of OTC ranging from 4.0 to 150 nM (Figure 1C), with a detection limit (3S/N) of 0.9 nM. In summary, both anodic “signal-on” and cathodic “signal-off” strategies are introduced to construct PEC aptasensors, and the fabricated sensors exhibited high sensitivity and selectivity, good reproducibility, and long-term stability.

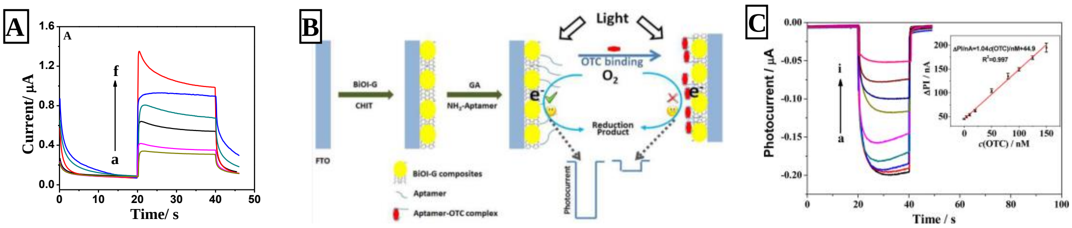

Figure 1. (A) Photocurrent responses of the aptasensor to (a-f) 1, 10, 20, 50, 80 and 100 nM SDM. (B) Schematic illustration of cathodic “signal-off” PEC aptasensor. (C) Photocurrent responses of the fabricated sensor incubated with different concentrations of OTC: (from a to i 0, 4, 10, 20, 50, 80, 100, 125, and 150 nM.) Inset: Calibration curve for OTC on the PEC sensor.

References

[1]. Yue, Z., Lisdat, F., Parak, W. J., et al. ACS Appl. Mater. Interfaces, 2013, 5, 2800-2814.
[2]. Okoth O. K., Yan K., Liu Y., et al. Biosens. Bioelectron., 2016, 86, 636-642.
[3]. Yan K., Liu Y., Yang Y., et al. Anal. Chem., 2015, 87, 12215-12220.

Electrochemical deposition and characterization of nickel oxide on nickel inverse opal structure for cathode of supercapacitors

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The templates of inverse-opal structure, which were prepared by electrophoretic self-assembly (EPSA) with polystyrene microspheres (diameter of 500 nm) and electrochemical deposition (ECD). A tripolar-electrode chemical station was employed to deposit the nickel oxide (NiO) thin films onto the nickel inverse opals templates via ECD process. Reagent grade sodium sulfate, sodium acetate and nickel sulfate were formulated into an electrodeposition solution. Both HNO_3 and NaOH were applied to modify the acidity of ECD solution. In this study, the ECD process parameters were consisted of current density, deposition voltage and deposition time. The capacitive characterization along with charge-discharge testing as well as microstructural analysis of Ni/NiO inverse opal specimens were carried out through cyclic voltammetry (CV), charge-discharge testing, and field emission SEM. SEM micrographs in Fig. 1 illustrates that Ni/NiO planar structure versus Ni/NiO inverse opal structure as supercapacitor's cathode, which formed with various deposition current density of 1~ 3 mA/cm^2. The results indicate the Ni/NiO inverse opal structure made with lowest current density had increased specific surface area, which resulted in a better specific capacity performance.

Keywords: inverse opal structure, electrochemical deposition (ECD), nickel oxide (NiO) thin films, tripolar-electrode electrochemical station, cyclic voltammetry (CV), electrophoretic self-assembly (EPSA).

1. J. P. Zheng, P. J. Cygan, T. R. Jow, et. al., J. Electrochem. Soc., **142** (1995) 2699-2703
2. X.H. Huang, et. al., Journal of Power Sources, **188** (2009) 588-591.
3. A.C. Sonavanea, et. al., Journal of Alloys and Compounds, **489** (2010) 667-673.
4. Mao-Sung Wu, et. al., International Journal of Hydrogen Energy, **32** (2007) 4153-4159.
5. V. Srinivasan and J. W. Weidner, J. of the Electrochem. Soc., **144** (1997) 210-213.
6. K. R. Prasad and N. Miura, Applied Physics Letters, **85** (2004) 4199-4201.
7. M. Carlen and R. Kotz, Electrochimica Acta, **45** (2000) 2483-2498.
8. Y. Sun, et. al., Materials Research Soc. Bulletin, **44** (2009) 227-230.
9. Guo-hui Yuan, et. al., Carbon, **43** (2005) 2913-2917.
10. V.D. Patake, et. al., Applied Surface Science, **255** (2009) 4192-4196.

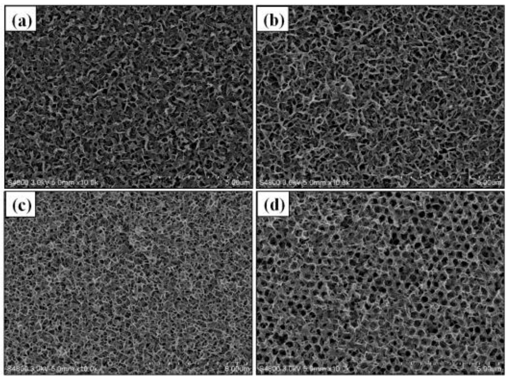

Fig. 1. SEM micrographs of (a) Ni/NiO planar electrode and (b~d) Ni/NiO inverse opal structure as supercapacitor's cathode. The samples exhibited here were formed with different deposition current density of (a) 3 mA/cm^2, (b) 3 mA/cm^2, (c) 2 mA/cm^2, (d) 1 mA/cm^2.

Electroless Pd membrane deposited on ultrasound-assisted-activated alumina support for hydrogen purification

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Inorganic membranes are potentially attractive for gas separations and catalytic applications at high temperature. The Pd/Al_2O_3 composite membrane exhibited good H_2/N_2 permselectivity and excellent thermal stability has received a growing interest to the separation and purification of hydrogen as well as to the catalytic membrane reactors in hydrogen-related petrochemical reactions[1-4]. In this work, the dense Pd membrane was prepared by the ultrasound-assisted activation followed by the electroless deposition of Pd on a porous α-alumina support. The distributions and morphologies of Pd nuclei on the α-alumina activated by conventional activation (c-Al_2O_3) and the α-alumina activated by ultrasound-assisted activation (u-Al_2O_3) were investigated. The ultrasound-assisted activation can uniformly disperse Pd nuclei on the porous Al_2O_3 support (Fig. 1). The Pd membrane on the u-Al_2O_3 support was dense and more uniform than that on the c-Al_2O_3 support, as shown in Fig. 2, and the H_2/N_2 selectivity of the Pd/u-Al_2O_3 composite membrane was higher than that of the Pd/c-Al_2O_3 composite membrane. The ultrasound-assisted activation pretreatments improved the deposition of Pd membranes on porous α-alumina supports and enhanced the H_2/N_2 permselectivity and thermal stability of the Pd/Al_2O_3 composite membrane.

Keywords: electroless deposition, Pd/Al2O3 composite membrane, ultrasound-assisted activation, hydrogen

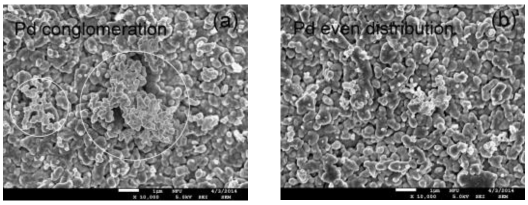

Fig. 1. The distributions of Pd nuclei on c-Al_2O_3 (a) and u-Al_2O_3 (b) supports.

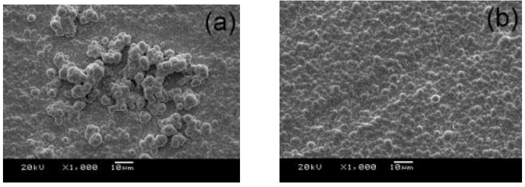

Fig. 2. The morphologies of Pd membranes on the c-Al_2O_3 (a) and u-Al_2O_3 (b) supports.

References:
1. A. Santucci, F.Borgognoni, M.Vadrucci, S.Tosti, J. Membr. Sci. 444 (2013) 378–383
2. M. Abdollahia, J. Yua, P. K.T. Liub, R. Ciorab, M. Sahimia, T. T. Tsotsis, J. Membr. Sci. 390 – 391 (2012) 32 – 42
3. F. Gallucci, E.Fernandez, P. Corengia, M. S. Annaland, Chemical Engineering Science 92 (2013) 40–66
4. W. X.Deng, X.H.Yu, M. Sahimi, T.T.Tsotsis, Journal of Membrane Science 451(2014) 192–204

Sequentially layer-by-layer growth of Ag(Cu) thin film using underpotentially deposition and self-limited redox reaction

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The conformal deposition technique is increasingly needed because a higher aspect-ratio trench/hole makes gap-fill capability more challenging when the device size is continuously scaled down. This work aims at using underpotential co-deposition Ag(Cu) alloy thin film by a wet electrochemical atomic layer deposition to meet the conformal deposition. Combining underpotential deposition (UPD) and self-limited redox reaction (SLRR) in electrochemical deposition, the Ag(Cu) alloy thin film can be prepared by carefully adjusting the concentration of mixed Ag and Cu electrolyte and the potential of deposition. Furthermore, using an underpotential deposition of sacrificial Pb metal and a self-limited redox reaction Ag(Cu) alloy in the process can also be used to control the film deposition as a layer-by-layer growth process. Figure 1 shows the current-potential-time curve of the layer-by-layer growth of Ag(Cu) film. A first UPD-Cu layer was deposited on the substrate at -100 mV, a subsequent UPD-Pb layer was deposited on the UPD-Cu layer at -520 mV. After that, SLRR-Ag(Cu) layer was growth by replacing the UPD-Pb layer at an open circuit potential in a mixed Ag and Cu electrolyte. Repeating the deposition cycle of UPD-Pb an SLRR-Ag(Cu), the Ag(Cu) film can be performed by using various electrolyte concentration ratios of Ag and Cu electrolyte. The results showed that Cu composition is in a range from 0 to 15 at.% by carefully controlling the concentration ratio of the Cu electrolyte and Ag electrolyte from 1 to 11. The lowest sheet resistance of 5.4 Ω/sq. can be obtained for Cu and Ag concentration ratio of 1. The film is thermally stable up to 600°C. The growth mechanism and the electrical properties of the resulting Ag(Cu) film will be discussed. By doing so, the feasibility of a low-resistive, high thermally stable, high electromigration resistance Ag(Cu) thin film will be explored to meet the requirement for interconnects.

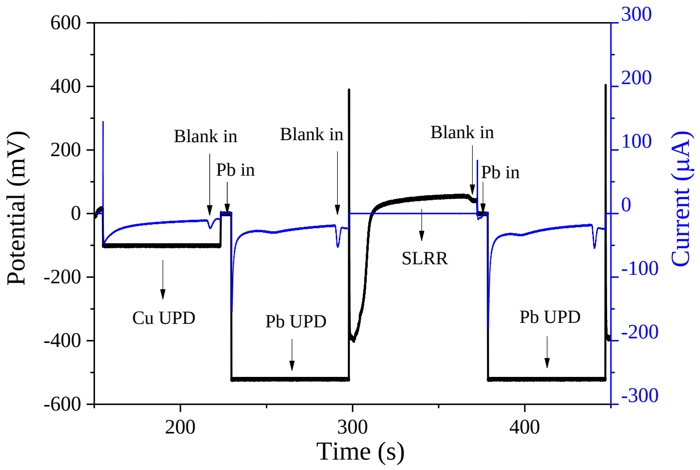

Fig. 1. Current-Potential-Time curves for Cu-UPD, Pb-UPD, and Cu-SLRR.

Enhancement of catalyst growth for electroless Cu plating of TaN barrier layer: the role of alkyl self-assembled monolayer

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Self-assembled monolayers (SAMs) are extensively used in microelectronic copper metallization primarily as seed-trapping layers, diffusion barriers, or pore-sealants for porous dielectric materials.[1–3] In contrast, direct electroless copper plating of nitride barrier layers assisted by a seed-trapping SAM is rarely examined. Therefore, TaN, an important component of barrier materials for Cu interconnect metallization, is selected here as a model substrate for a new seeding (nickel catalyst formation) process of electroless Cu plating. The process flow involves substrate pretreatments from hydroxylation (piranha etching), octadecyltrichlorosilane SAM (OTS-SAM) growth and subsequent functionalization (Fig. 1). Catalytic particles (seeds) upon adsorption onto piranha-treated (reference) TaN layers via Ta–OH linkages tend to agglomerate, resulting in a limited seed density of 8×10^{13} m^{-2}. In contrast, those adsorbed on piranha-treated (hydroxylated) TaN layers with a plasma-functionalized OTS monolayer are free from agglomeration and have an average size of 3 nm, along with a high seed density of 1×10^{15} m^{-2}. X-ray photoelectron spectroscopy, together with transmission electron microscopy, clearly identifies the thin-film materials deposited and functional groups induced by each of the pretreatments. Finally, the mechanism of seeding enhancement will to be clarified, and the enhancement of seeding to benefit electroless copper plating will be demonstrated.

1. P. Lu, Z. Shi, and A. V. Walker, Langmuir, 27, 13022 (2011).
2. Y. Chung, S. Lee, C. Mahata, J. Seo, S. M. Lim, M. S. Jeong, H. Jung, Y. C. Joo, Y. B. Park, H. Kim, and T. Lee, RSC Adv., 4, 60123 (2014).
3. Y. T. Sun, M. Krishtab, H. Struyf, P. Verdonck, S. De Feyter, M. R. Baklanov, and S. Armini, Langmuir, 30, 3832 (2014).

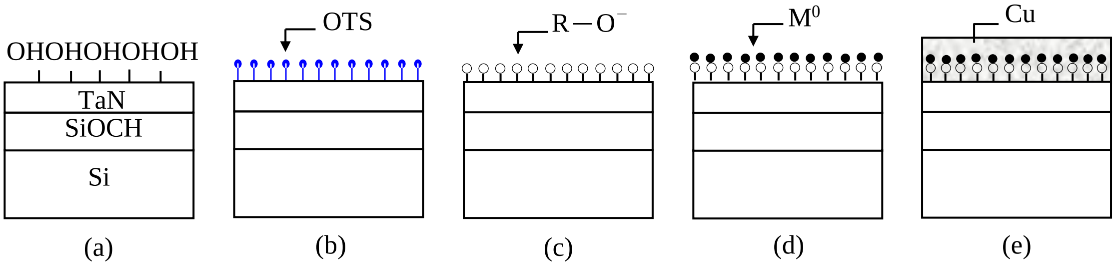

Fig. 1. Process steps for sample preparation: (a) TaN hydroxylation, (b) OTS-SAM growth, (c) OTS-SAM functionalization, (d) catalyst growth, and (e) electroless Cu plating.

Electrophoretic Deposition OF Diamond-Like Carbon (DLC) Onto Silicon Nanowires

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Abstact

Diamond-like carbon (DLC) films have been deposited onto Silicon nanowires (SiNWs) by electrophoretic method using a dimethyl sulfoxide (DMSO) organic solution as electrolyte at low voltages (50-200V). The effect of bias voltage, deposition time and the SiNWs length on morphological properties has been studied. The morphological and structural properties of the films have been investigated using scanning electron microscopy (SEM), X-rays diffraction (XRD) and Raman spectroscopy, respectively. It has been found that the DLC films are compact and composed of spherical grains with a mean size of about 0.2 µm. In addition, it has been noted that the XRD spectrum is dominated by intense peaks of diamond and graphite. This result has been confirmed by Raman analysis which shows the spectrum is mainly composed of amorphous carbon where a broader band in the range from 1000 to 1800 cm-1 has been observed.

Keyswords : Diamond-like carbon (DLC), electrophoretic, silicon nanowires.

Great Performance of Ultra-Thin Orientated $BiFeO_3$ Films Deposited by Atomic Layer Deposition

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Highly (001)-orientated $BiFeO_3$ ultra-thin films with total thickness less than 10 nm were deposited on Si (001) substrates by atomic layer deposition (ALD) with a $LaNiO_3$ buffer. For comparison, a RF sputtering sample with the same thickness also has been prepared. The ALD combined with interrupted flow method and exchange reaction between Bi and Fe precursors which can provides a better growth method for ternary compounds. The x-ray diffraction investigated the crystalline and the only phase in the film was $BiFeO_3$ with the deposition temperature lower than 550ºC. Synchrotron X-ray diffraction anomalous fine structure also certified well valence bonding through $BiFeO_3$ (001) diffraction peak. The stoichiometric of $BiFeO_3$ got from XPS indicated ALD has much better proportion ratio than RF and this is also in agreement with DAFS results. The HRTEM cross-section view shows a conformal and uniform deposition on the top of LNO buffer layer as shown in Fig. 1a.

In the results, the $BiFeO_3$ thin film deposited by ALD shows excellent leakage for at least 1000 times improvement respect to RF as shown Fig. 1b, which is suitable for ferroelectric random-access memories devices fabrication. The highest remanent polarization value was observed from the hysteresis loop with $2Pr = 2.0\ \mu C\ cm^{-2}$. This remanent polarization shows a strong correlation with rate of growth; the greatest crystalline quality appeared with a growth rate near the theoretical value at an appropriate temperature. The complete mixed ternary BFO grown with ALD at an appropriate rate also involved a growth of O-Fe-Bi atoms layer by layer reflecting an effective stoichiometry and valence bonding in measurement. This advantage is really beneficial for IC fabrication using a film thickness monitor in situ such as a quartz crystal microbalance sensor. In this work, we clearly demonstrate a new capability to achieve a uniform fabrication of a large area and show a satisfactory performance of BFO materials to create a new application in the electroceramics field.

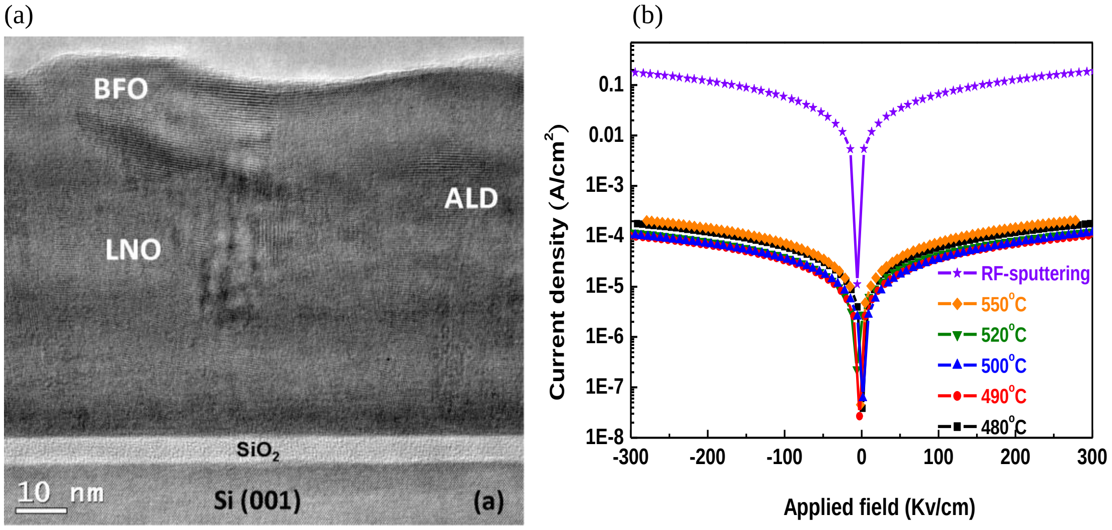

Figure 1: BFO thin films growth on LNO buffer layer for (a) Cross-section view of HRTEM; (b) J-E curves of the BFO thin films with different substrate temperatures